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PHOTOLYTIC RING CLEAVAGE OF 1,2-DIARYLCYCLOPROPANES WITH BROMINE IN A NON-POLAR SOLVENT

by

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[redacted]

Submitted in partial fulfillment
for the degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

from the

UNITED STATES NAVAL POSTGRADUATE SCHOOL
August 1966

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ABSTRACT

This work studied further the well established analogy between cyclopropanes and olefins. A series of 1,2-diarylcyclopropanes were prepared and were characterized by their ultraviolet, infrared and NMR spectra. Some of these compounds have not previously been reported.

Reactions of these compounds were studied under dark and photolytic conditions with bromine in carbon tetrachloride. No reaction was observed under dark conditions while addition of equimolar amounts of bromine took place under photochemical conditions. The addition product in all cases was the 1,3-dibromo-1,3-diarylpropane.

The kinetics of this reaction were studied at low concentrations (0.003 molar) and the influence of the para-substituent on the rates of reaction determined. The reaction rates plotted against Hammett sigma values were linear and gave a rho of -0.49 for the cis isomers and a rho of -0.44 for the trans isomers. The rate equation under these conditions was found to be

$$\text{rate} = k(\text{cyclopropane})(\text{Br}_2)^{\frac{1}{2}}.$$

A mechanism is proposed for the reaction under these conditions.

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INTRODUCTION

The synthesis and physical and chemical properties of cyclopropanes have long attracted the interest of many chemists. The interest has been derived from the similarities that many cyclopropanes have with analogous olefins. These similarities appear in an examination of the physical as well as the chemical properties of these compounds. The classic criteria of unsaturation in a compound is the participation in addition reactions. That many cyclopropanes take part in addition reactions has been frequently demonstrated. In this work some aspects of these similarities were to be examined.

To explore further this analogy a series of 1,2-diarylcyclopropanes were prepared. The spectral properties of these compounds were examined and compared with the similar olefins. A series of reactions of bromine in carbon tetrachloride with these compounds were carried out. Both the dark reaction and the photochemical reaction were studied. Comparative rates of reaction between the differently substituted cyclopropanes were examined for the photolytic reaction.

HISTORICAL

Part I

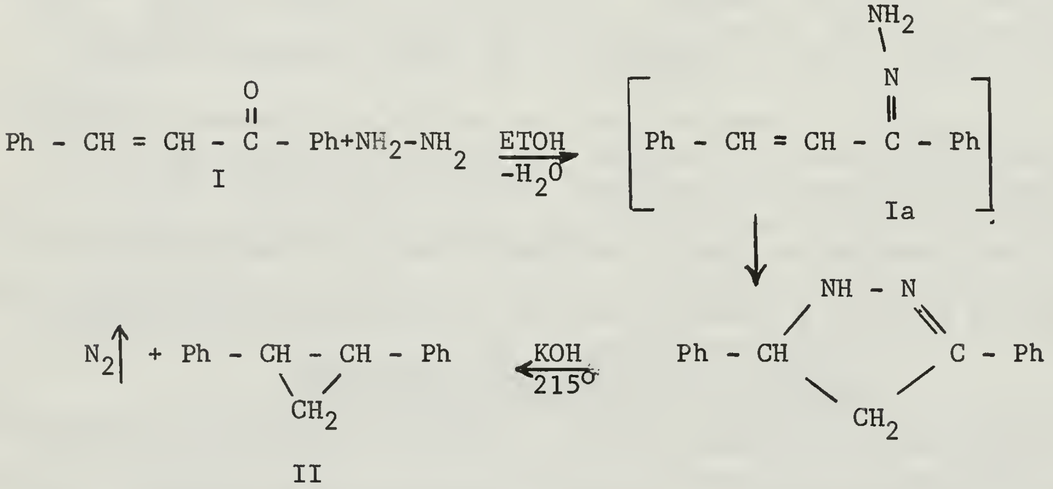
The chemistry of cyclopropane and its derivatives has interested chemists for many years. The rather unexpected chemical and physical properties of cyclopropane derivatives, especially the aromatic ones, set these compounds apart from the other cycloalkanes. A typical example is the bathochromic shift observed in the carbonyl absorbtion spectrum of α, β-unsaturated ketones which is also observed (to a lesser extent) for cyclopropyl ketones. Cyclobutyl and higher analogs do not show this same ability to conjugate to any extent with π electrons. Similar conjugation is observed when the series ethyl benzene, styrene, and phenylcyclopropane are compared. In what follows will be (1) a review of the important synthetic techniques and (2) an examination of some of the known ring opening reactions of substituted cyclopropanes.

Synthesis of Cyclopropane Derivatives

Of the numerous methods (86,106) which are available for the synthesis of cyclopropanes, five general categories can be formed. These are (1) pyrolysis of 1- and 2-pyrazolines; (2) dehydrohalogenation of alkyl halides containing an active methylene group; (3) intramolecular Wurtz type reaction on 1, 3-dihalo compounds; (4) addition of carbene to olefins; and (5) miscellaneous condensation and elimination reactions.

Cyclopropanes from Pyrazolines

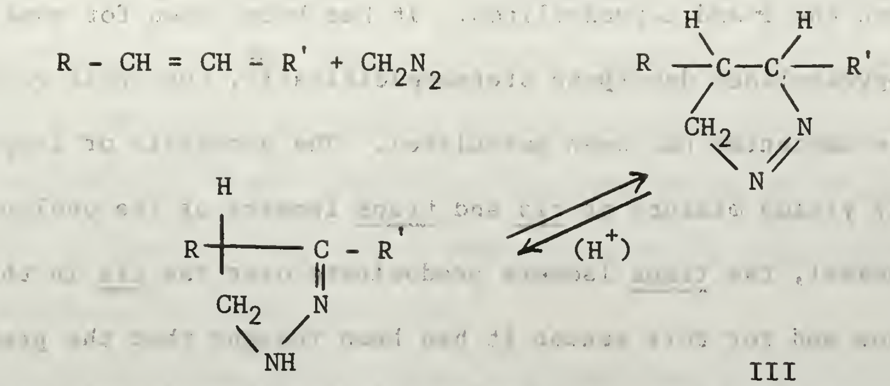
One of the more widely used preparative techniques for alkyl and aryl substituted cyclopropanes is the base pyrolysis of 2-pyrazolines. This method, originated by Kishner (51) during the early 1900's, consists of the addition of hydrazine to an α, β-unsaturated aldehyde or ketone to give the 2-pyrazoline. Pyrolysis, by dropping the pyrazoline on platinized asbestos at 250°C, yielded the desired cyclopropane. More recently (52) pyrolysis has been shown to take place using a mixture of powdered potassium hydroxide and copper bronze at 215°C. Some cases of pyrolysis in the absence of any catalyst have also been observed for alkyl substituted 2-pyrazolines (46). The use of this technique for the preparation of isomeric 1, 2-diphenylcyclopropane (II) from 1, 3-diphenylpropenone (I) is illustrated below. Much evidence (7) exists that indicates that the pyrazoline formation follows the preliminary formation of a hydrazone (Ia).



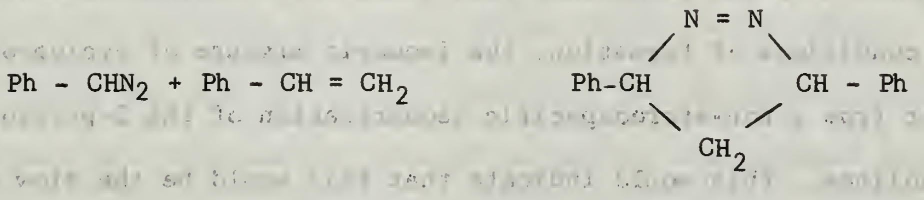
(3, 5-diphenyl-2-pyrazoline)

Pyrazolines may also be prepared from diazo compounds with α, β unsaturated esters and α, β unsaturated ketones (2). With olefins and diazomethane, initially the 1-pyrazoline (III) is formed. Depending on the relative stabilities this compound may or may not rearrange to the corresponding 2-pyrazoline (IV). In some cases, isomerization can be brought about by treatment with dilute acid, in others, it occurs sponteneously.

The addition of a substituted diazomethane to an olefin also may yield 1-pyrazolines. The addition of phenyldiazomethane (V) to styrene gives trans 3, 5-diphenyl-1-pyrazoline (VI) (74). Decomposition occurs



IV III

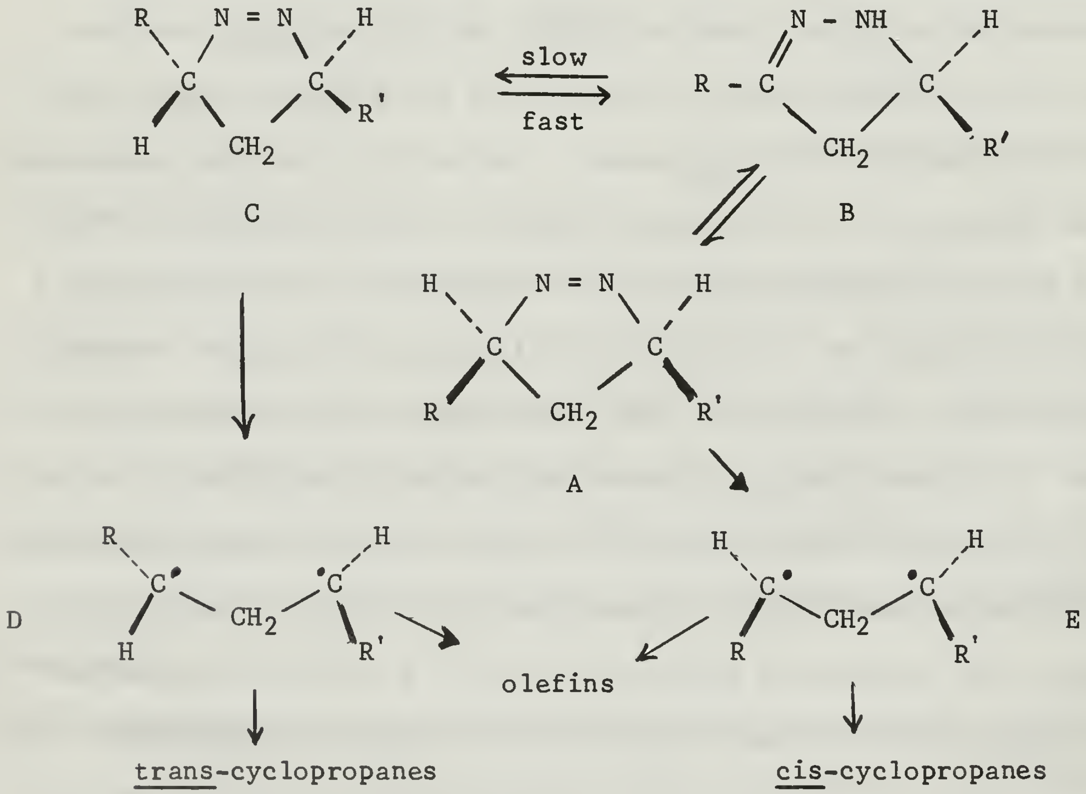


V VI

readily in refluxing benzene to give quantitive yields of trans-1, 2-diphenylcyclopropane. (The addition of p-methoxyphenyldiazomethane to p-methoxystyrene yields a mixture of both the cis and trans 1-pyrazoline.) (75) It appears that the influence of the p-methoxy group brings about the formation of the cis isomer. The currently accepted mechanism for the formation of 1-pyrazolines involves concerted addition to the alkene by the diazomethane group. (40). Overberger (75) has postulated a stepwise mechanism for the formation of 1-pyrazolines and the specific mechanism that is operative in each case depends on the reactants involved. More specifically, it seems that as the nucleophilicity of the olefin increases the mechanism may be viewed more as a stepwise addition.

Pyrazolines may also be prepared from β substituted aldehydes and ketones. (43) Addition of phenyl-hydrazine to a carbonyl compound with a β-halogen or β-dialkylamino group usually yields the 2-pyrazoline. (25).

Considerable controversy exists regarding the mechanism of decomposition of both the 1- and 2-pyrazolines. It has been known for some time that most 1-pyrazolines decompose stereospecifically, but until recently no reasonable mechanism had been postulated. The pyrolysis of 2-pyrazolines usually yields mixture of cis and trans isomers of the cyclopropane. In general, the trans isomers predominate over the cis in these decompositions and for this reason it had been thought that the predominant cyclopropane was determined by its relative thermodynamic stability. However, Jones (45) has postulated that since the cyclopropanes are stable under the conditions of formation, the isomeric mixture of cyclopropanes must result from a non-stereospecific isomerization of the 2-pyrazolines to 1-pyrazolines. This would indicate that this would be the slow step in the decomposition of 2-pyrazolines. A free radical mechanism incorporating these postulates has been proposed (41,74) and is shown below.



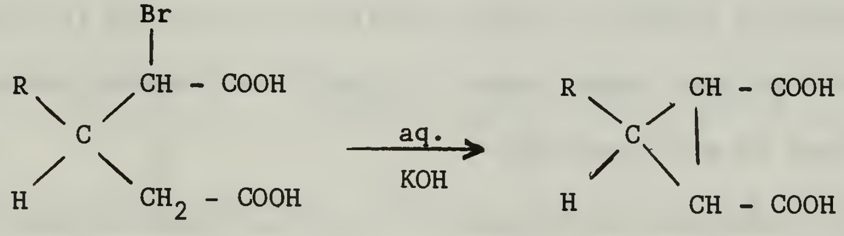
In general, the stereochemistry of cyclopropanes resulting from the decomposition of both 1- and 2-pyrazolines depends not only on the structure of the parent pyrazoline but also on the stability of intermediate biradicals (D and E above) at the temperature of the pyrolysis. Both EPR and kinetic studies have shown evidence for the existence of these biradical intermediates. (18).

In most cases pyrazolines yield cyclopropanes in relatively high yields. Major competitive reactions are rearrangements and olefin formations during pyrolysis which may reduce yields considerably. Additional losses may also occur by oxidation of the pyrazoline (43). Some pyrazolines are sufficiently reactive to ignite when exposed to air, others react with oxygen to give a complex mixture of products.

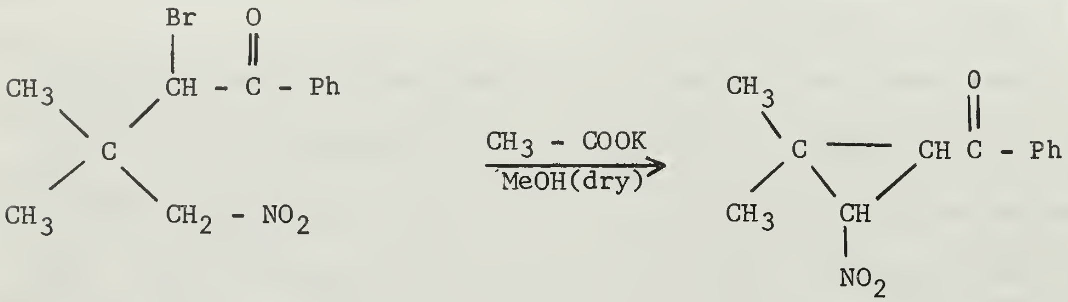
Cyclopropanes by Intramolecular Dehydrohalogenation

Compounds containing an active hydrogen atom with a halogen atom beta to it readily undergo dehydrohalogenation to give cyclopropanes. Various electonegative and anion stabilizing groups have been used to provide an active methylene group. Not only is the acidity of the proton important but also the stability of the carbanion for this type of elimination. Adjacent carboxyl groups have been used most frequently along with nitro, cyano and ester groups.

A typical example of this type of synthesis is illustrated below using aqueous basic conditions. A yield of forty-seven percent has been



reported for this reaction (41). Using gammabromonitroalkanes, nitro-substituted cyclopropanes have been prepared (53). Smith and Englehardt (94) have used this technique to prepare a series of nitrosubstituted-cyclopropanes. Yields of seventy-five percent and higher are common for this type of elimination.



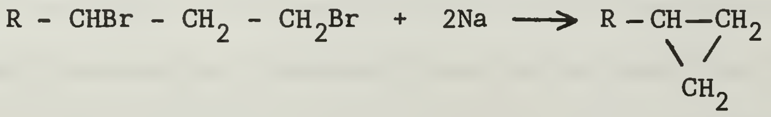
Nitriles also have been used to provide a sufficiently reactive hydrogen for cyclization reactions. Gamma-halonitriles eliminate to give cyano-substituted cyclopropanes in good yield (88). Hydrolysis then yields cyclopropyl ketones. Similar starting materials were used by Bruylants (10) to produce cyclopropyl ketones using methyl Grignard. Overall yields of 60% were obtained for several alkyl cyclopropyl ketones.

The action of sodium on neopentyl halides will yield cyclopropanes in fair yields. Whitmore et.al. (111,113) obtained 36% of 1, 1-dimethylcyclopropane on treating neopentylchloride with sodium. Lower yields (13%) of the cyclopropane are obtained with the neohexyl analog in this Wurtz type reaction.

The synthetic utility of these elimination reactions is, however, questionable. In most cases, higher yields of the desired cyclopropane may be obtained by other methods.

Synthesis of Cyclopropanes via Freund and Gustavson Reactions

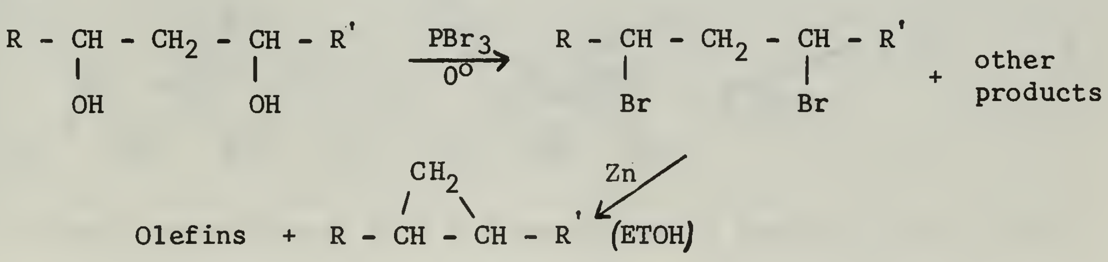
Both the Freund (Wurtz reaction applied to ring closure) and Gustavson reaction have been used extensively in the preparation of alkyl-and aryl-cyclopropanes (86). The Freund reaction involves the action of sodium on 1, 3-dihalo-compounds as illustrated below.



Although the yields vary from poor to fair for this type of reaction, contamination from side reaction products limits the usefulness as a synthetic preparation.

The Gustavson reaction (action of zinc dust on 1, 3 dibromo-compounds) can give high yields of cyclopropanes (3). The yields vary depending on the type of dibromide employed. In order of decreasing yields are the di-bromides primary-primary, primary-secondary, and secondary-secondary starting materials. The reactions are typically carried out in alcohol and at reduced temperature on dibromides prepared from the appropriate diol.

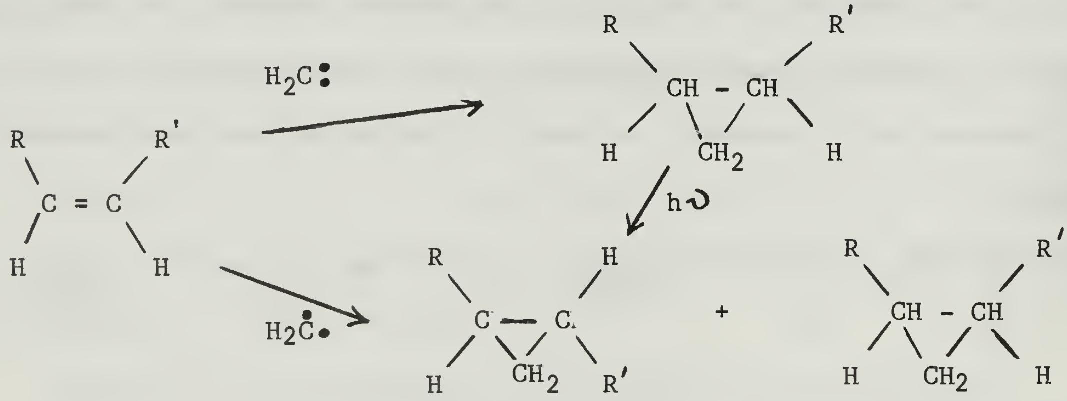
Poor yields are usually obtained from tertiary dibromides with most of the product being the corresponding olefin (90). A series of alkylcyclopropanes has been prepared by this method (47). Arylcyclopropanes may also be prepared by this technique if the appropriate dibromide can be obtained. However, the action of phosphorous tribromide on many alpha-gamma-diols brings about rearrangements while other dibromides have been too unstable to be prepared. An overall reaction scheme is illustrated below.



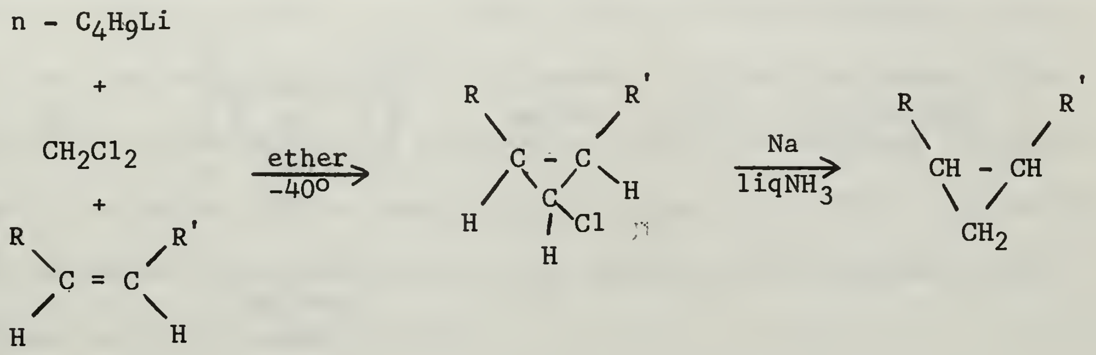
Cyclopropanes from Carbene Reactions with Alkenes

In more recent years cyclopropanes have been prepared to a great extent by the addition of divalent carbon to olefins. In view of the many general references (12,37) available on the formation and reaction of methylenes, only some of the more important cyclopropane syntheses will be examined here.

Photolysis of diazomethane in the gas or liquid phase in the presence of an olefin leads to a cyclopropane of the same geometrical configuration as the starting olefin (24). The inference drawn is that the methylene formed is a singlet rather than a triplet. Other gas phase reactions have shown the presence of triplet methylene which does not give stereospecific addition to olefins (28). This lack of stereospecificity has also been shown to arise from isomerization of excited state cyclopropanes after the addition of either singlet or triplet methyene to an olefin. In general, for methylenes, the addition to an olefin to form a cyclopropane varies as to stereospecificity depending on reaction conditions. Methylene produced by photolysis of ketene or dehydrohalogenation of a methyl halide (29) gives essentially the same results. An illustration of these reactions is given below.

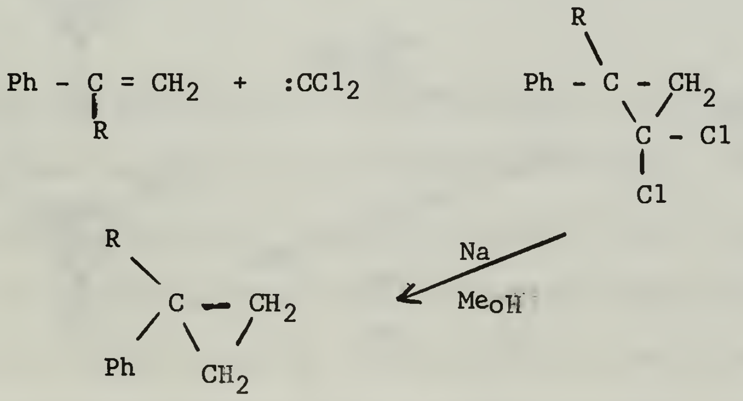


Many of the reactions of methylenes are also possible with dihalo-methylenes and monohalomethylene. Closs (13) obtained high yields of various alkylchlorocyclopropanes by the addition of monochlorocarbene to olefins. The monochlorocarbene was generated from n-butyllithium and methylene chloride in the presence of the olefin (below).

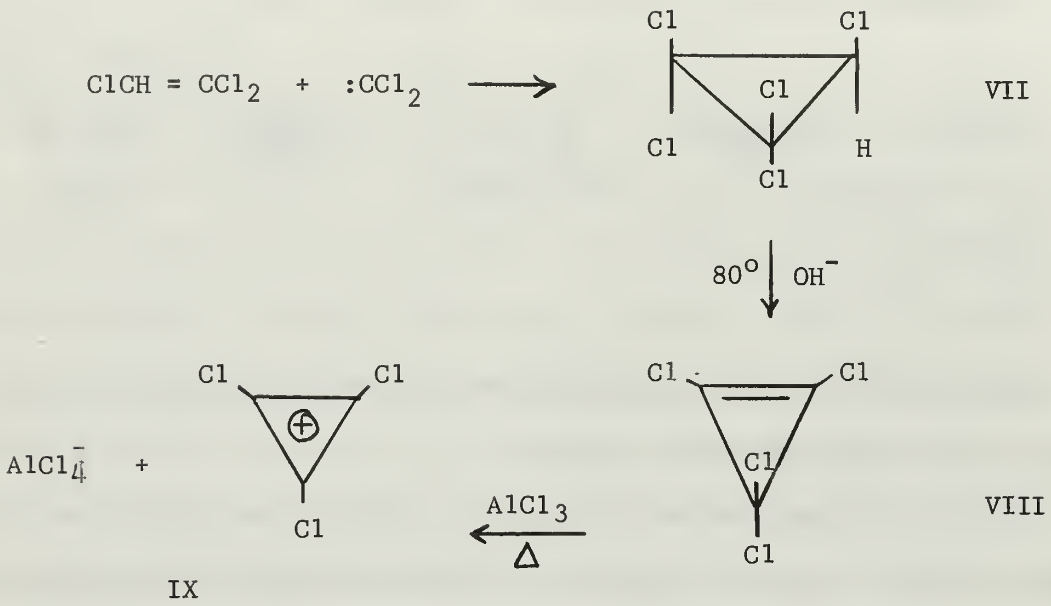


The hydrocarbon is readily obtained from the chlorocyclopropane by reduction with sodium in liquid ammonia.

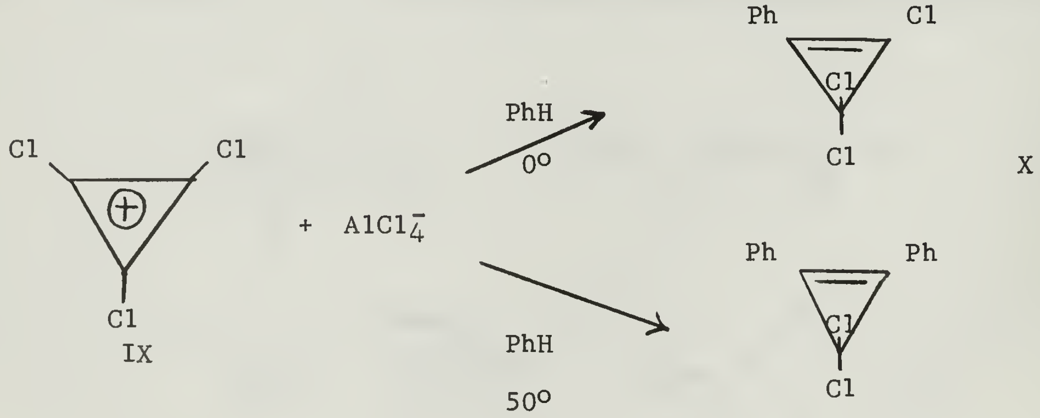
Dichlorocyclopropanes can be readily prepared from olefins and dichlorocarbene. In this instance the dichlorocarbene is generated in the presence of the olefin by alkaline hydrolysis of chloroform. Styrene and *alpha*-substituted styrenes have served as carbene acceptors for both dichloro-and dibromocarbene (21). The resulting *gem*-dihalocyclopropanes are readily reduced to give the aromatic cyclopropyl hydrocarbon. Overall yields of 70-80% have been obtained.



Tobey and West (102, 103) have described the synthesis of aryl substituted cyclopropanes. A series of reactions are involved beginning with the addition of dichlorocarbene to trichoroethylene to give pentachlorocyclopropane (VII). Dehydrohalogenation gives tetrachlorocyclopropene



(VIII). Treatment with $AlCl_3$ and heat yields the trichlorocyclopropenium ion(IX). In the presence of benzene and substituted benzenes, (IX) reacts to give arylcyclopropenes (X) which can be further reduced to the cyclopropanes.



More recently it has been shown that cyclopropanes themselves can serve as carbene sources (80). Photolysis of phenylcyclopropane or dibenzonorcaradiene in the presence of olefins with ultraviolet light gives carbene addition to the olefin.

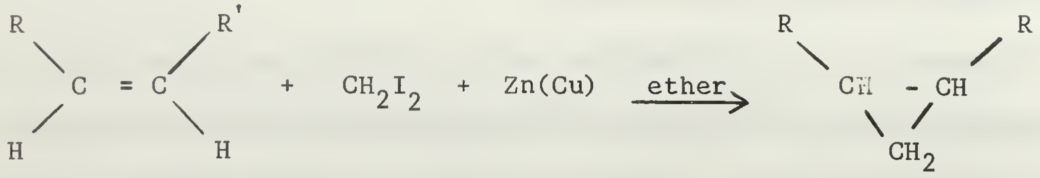
In general, the use of carbene, monohalocarbene and dihalocarbene in a synthetic route to substituted cyclopropanes results in clean reactions with high yields. Only small amounts of carbon-hydrogen insertion are observed and frequently no isomeric olefins are formed along with the cyclopropanes. The reactivity of the above carbenes has been found to decrease with increasing halogen substitution (15). Therefore less extensive side reactions are to be expected with mono-and dihalocarbene than with carbene itself.

A considerable number of substituted methylenes have been prepared (37). In many cases the actual evidence for the presence of methylene has been scanty. Reaction mechanisms using carbanions as intermediates rather than carbene intermediates often are equally as plausible. For the most part these substituted carbenes give poor yields of cyclopropanes and have found little use in synthetic reactions.

Miscellaneous Synthetic Routes to Cyclopropanes

In addition to the above general categories for the synthesis of cyclopropanes many other types of reactions have been used. With some exceptions noted below, none of these apply as a general synthetic technique.

Simmons and Smith (93) in 1959 introduced a sterospecific organometallic general synthesis of cyclopropanes. A wide variety of cyclopropanes have been prepared in good yields from this reaction of an olefin, diiodomethane and an active zinc-copper couple (59). The simplicity of the reaction, ready availability of starting materials and purity of the products make this the method of choice for the synthesis of most alkyl cyclopropanes. The reaction is illustrated below.



Although the mechanism of the reaction has not been completely elucidated a reactive carbene intermediate appears unlikely while an organometallic complex seems plausible.

Alkyl cyclopropanes have been prepared in low yields by deamination reactions (91). Treatment of 3-methyl-2-aminobutane with acetic acid at 56° gave in addition to the 1-and 2-olefins 15% of a mixture of cis and trans 1, 2-dimethylcyclopropane.

The reaction of quaternary ammonium halides with sodium amide in liquid ammonia has given good yields of arylcyclopropanes (11). Both phenyl and 1, 1-diphenylcyclopropane have been prepared in 80% yield using this technique.

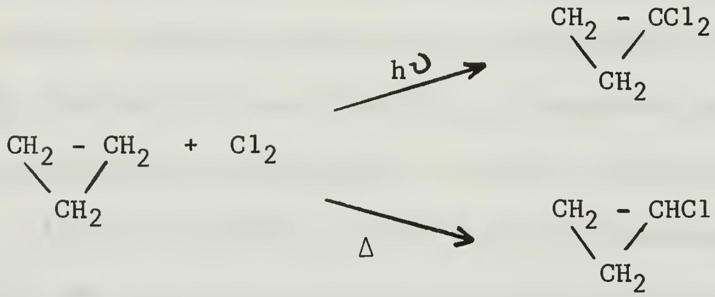
HISTORICAL

Part II

The chemistry of cyclopropane and its derivatives has provided a source for many theoretical descriptions of the bonding in these three-membered ring compounds. Higher alicyclic compounds such as cyclobutane and cyclopentane and their derivatives for the most part exhibit only properties characteristic of alkanes. Cyclopropane and its derivatives exhibit properties of alkanes as well as many properties associated with alkenes. Coulson and Moffitt (16,17) and Walsh (108) have examined the nature of cyclopropanes and put forth possible descriptions of the bonding of these compounds. Although these descriptions and those of others are somewhat different, there seems to be general agreement regarding the p-character of the bonding molecular orbitals. Some of the properties and reactions described below will point out this p-character and the ability of cyclopropanes to conjugate with adjacent pi bonds. In nearly all instances, cyclopropanes are found to have properties intermediate between the corresponding alkene and alkane.

Many of the earlier workers examined reactions with cyclopropane itself and compared the results with other cycloalkanes and alkenes. Ogg and Priest (69,70) examined extensively the reactions of bromine and iodine with cyclopropane. At room temperature bromine reacts photochemically with cyclopropane in the vapor phase to give exclusively 1, 3 dibromopropane. In the dark at higher temperatures (220^o) substitution occurs along with addition to give a mixture of products. Kharasch and his co-workers (49) have examined the effect of light and oxygen on the addition of HBr and bromine to cyclopropanes. Their observations show that pure bromine and pure cyclopropane do not react appreciably in the dark and only slowly in the light in the absence of oxygen. The presence of minute amounts of oxygen is effective in initiating a photochemical chain reaction between bromine and cyclopropane. Similar catalytic effects were observed using organic peroxides.

Reactions of cyclopropane with chlorine and iodine have also been examined. Chlorine reacts with cyclopropane photochemically to give substitution products (82) and no ring opening products. Substitution products are also observed for high temperature reactions of chlorine and cyclopropane in the absence of light as shown below.



Although the reactions of iodine with cyclopropane have not been studied as extensively as bromine and chlorine reactions, the formation of a molecular compound (1:1) has been observed (27). Similar adducts have been observed for some low molecular weight alkenes.

The catalytic hydrogenation of cyclopropane has been studied extensively using various reaction conditions.[1] Platinum black, nickel on pumice and palladium are but a few of the catalysts used at atmospheric pressure. Hydrogenation under these conditions requires temperatures of 50° and higher.

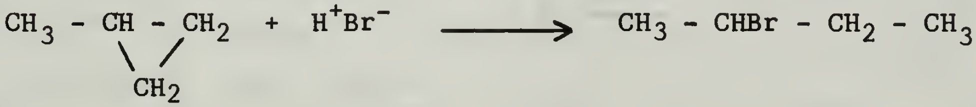
More interest, however, has centered on the alkyl and aryl substituted cyclopropanes than on cyclopropane itself. Most of the reactions observed and spectral studies undertaken have been for the purpose of comparison with structurally similar alkenes. Where direct comparisons are available the cyclopropanes are generally found to react in a manner similar to that of the corresponding alkene albeit usually slower.

---

[1] For leading references see Lukina (90).

Kohler and Conant (55) examined the reactions of alkyl, aryl, and carbonyl substituted cyclopropanes in aqueous media with hydrogen chloride and hydrogen bromide. Alkyl cyclopropanes react in accordance with Markownikoff's rule in the same manner as alkyl substituted alkenes as shown below.

$$CH_3 - CH = CH_2 \quad + \quad H^+Br^- \longrightarrow CH_3 - CHBr - CH_3$$



Turnbull and Wallis (104) have examined the kinetics of the reactions between bromine and a series of carboxylic acid cyclopropane derivatives. The reactions were carried out in aqueous acetic acid in amber bottles

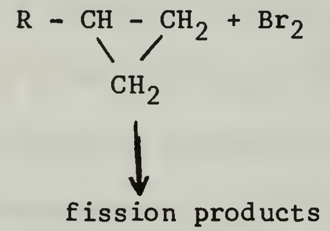
$R = -COOH$

$R = -CH_2COOH$

$R = -CH_2CH_2COOH$

$R = -CH_2CH_2CH_2COOH$

$R = -CH_2CH_2CH_2CH_3$



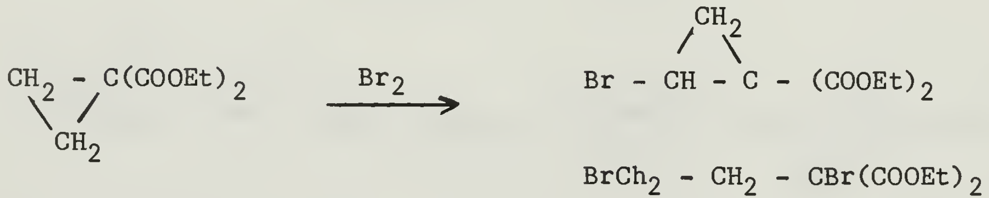
at three different temperatures. The general reaction kinetics were similar to those obtained for a similar series of olefins (26). Their results led them to postulate the following mechanism.

$$\begin{tikzcd} \text{Cyclopropane} + Br_2 \arrow[r] & \left[Br_2 - \text{cyclopropane} \right] \arrow[d] \\ & \text{fission products} \end{tikzcd}$$

The addition of bromide ion leads to a depression in the rate due to the following equilibrium.

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

Nicloet and Sattler (68) examined the action of bromine on carboxylic acid substituted cyclopropanes when the bromination was carried out at 40°-50°. The reactions vessels were illuminated with a high intensity quartz mercury lamp. A mixture of products was obtained as indicated below. The monobromo product XI was also shown to react with HBr to give the dibromo product XII. On the basis of this reaction it was felt that XII arises not only from direct addition of bromine to X but also from the addition of HBr produced in the substitution of X to give XI.



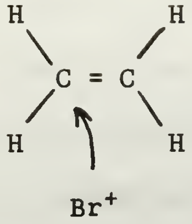
X

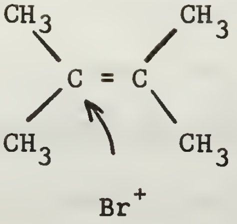
XI

XII

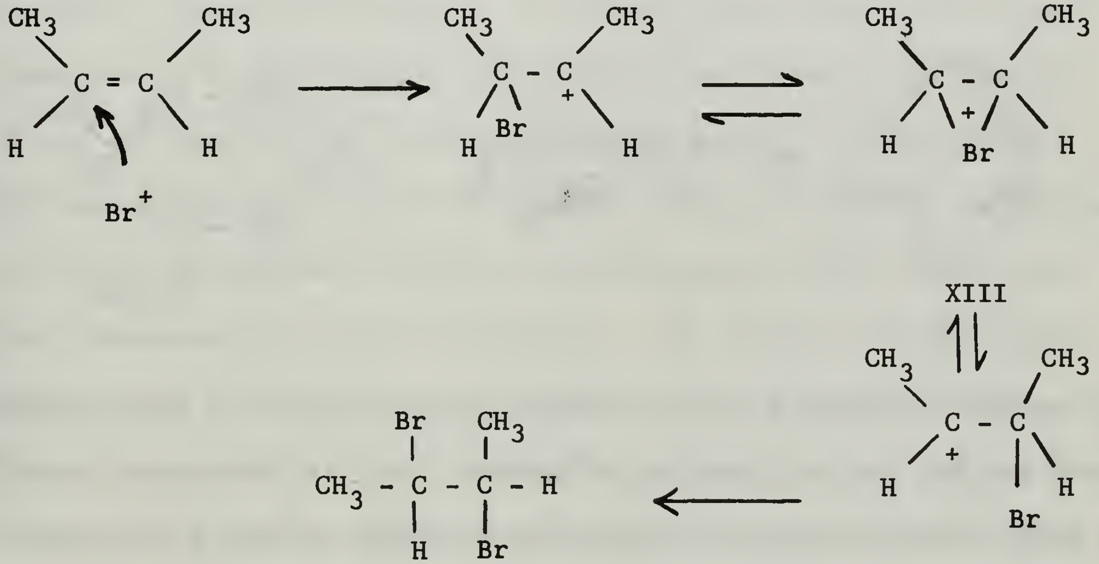
More recently a series of methyl and ethyl substituted cyclopropanes has been examined using a bromometric method (64). No attempt was made to study the mechanism of addition or to identify the products of reaction. The cyclopropanes were reacted in the dark with bromine and the percent reacted determined at several time intervals. These results were very similar to the results obtained on analogous olefins although more vigorous conditions for ring opening are required.

The effect of alkyl substituents was shown to be substantially the same for the cyclopropanes as for the related olefins. Ingold (42) found that bromine adds to tetramethyl ethylene 14 times more rapidly than to ethylene in methylene chloride at -78°. The mono, di- and tri-methyl



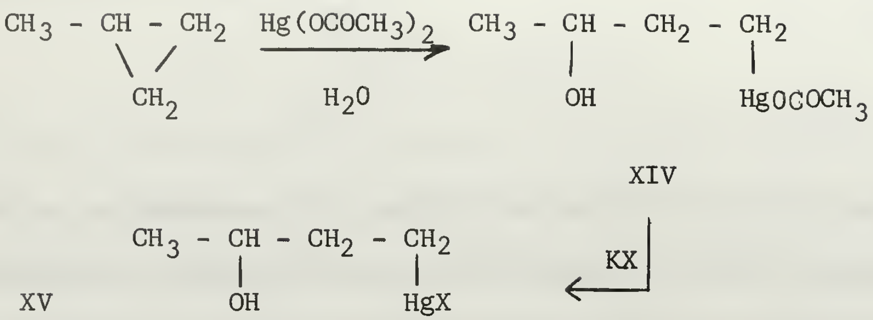


substituted ethylenes had intermediate values. The explanation of this lies in a mechanism using a bromonium ion as the electrophilic attacking agent at the double bond. The attack is facilitated by the increased electron density on the carbons of the double bond as the number of methyl groups increases. Where geometric isomers of alkenes are used the addition is found to be trans. Roberts and Kimball (83) have put forth a mechanism using a cyclic intermediate (XIII) followed by attack of Br^- to give the trans-addition product (XIIIa)


XIII

(d,l mixture)

Similar ring opening reactions have been carried out on alkyl cyclopropanes using aqueous mercuric acetate (60). The cyclopropanes reacted to give alpha-gamma reaction products (XIV). These mercuric acetates were further reacted with potassium chloride to give the gamma mercurated alcohols (XV).

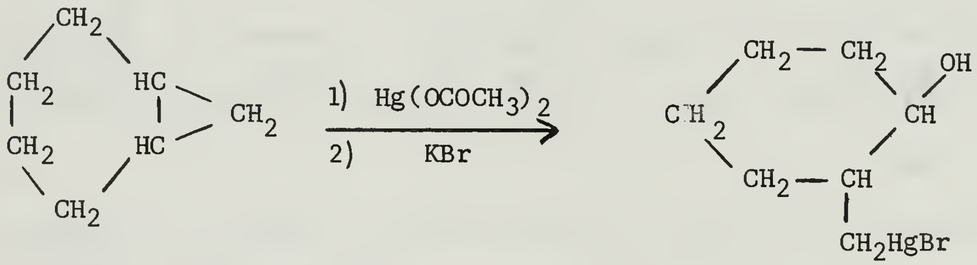


XIV

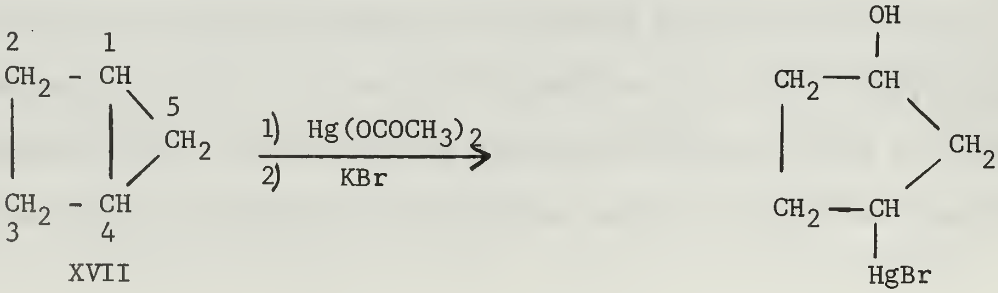
XV

In all cases examined the cyclopropane was found to open between the most highly and least highly alkyl substituted carbons.

In bicyclic compounds containing a three-membered ring similar results have been obtained when no four-membered rings are present (57). For example bicyclo-(4,1,0)-heptane (XVI) reacts with mercuric acetate to open the three-membered ring between the most and least highly substituted carbons. However in bicyclo-(2,1,0)-pentane (XVII) the bond breakage occurs between the two substituted carbons. This is undoubtedly due to the highly strained nature of this bond belonging to both a three-and four-membered ring and the reaction results in the maximum release of



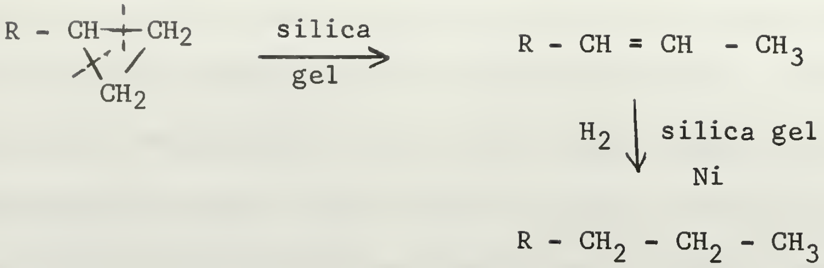
XVI

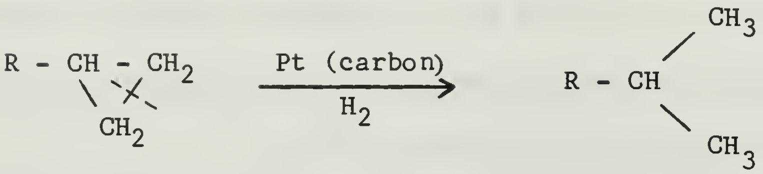


XVII

strain. This is in contrast to the statistically favored and electronically favored factors for opening between carbons 1 and 5 or carbons 4 and 5. Bicyclic systems containing a three-membered ring have also been examined in this regard using lead and thallium acetates, p-toluenesulfonic acid and bromine (57). In each of these cases the predominant reaction is the opening of the carbon-carbon bond, 1-4, in XVII above. However, some of these reactions give substantial amounts of other products. The product distribution appears to be related to the electronegativity of the attacking electrophile (101).

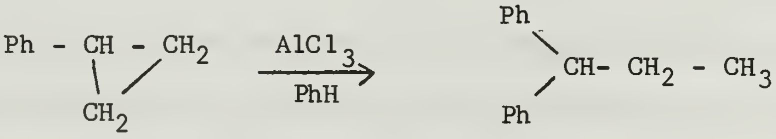
The most widely studied ring opening reaction of alkyl- and arylcyclopropanes is hydrogenation. Earlier workers were at odds over the direction of ring opening. Kishner (50) and others observed hydrogenation taking place with rupture of the bond between the two carbons having the greatest number of hydrogens. Kelso _et al._ (48) found in all cases studied that the carbon-carbon bond was ruptured between the carbons carrying the greatest and least number of hydrogens. These contradictory results have been shown (65) to be due to the concurrent isomerization of the cyclopropane followed by hydrogenation of the alkene and direct hydrogenation of the cyclopropane. The amount of isomerization depends on the catalyst used. Kieselguhr, silica gel and aluminum oxide give nearly 100% isomerization when used with nickel. These reactions are illustrated below. The hydrogenation of aryl substituted and conjugated cyclopropanes occurs more readily than with non-conjugated cyclopropanes. In addition where geometric isomers are possible the _trans_ isomers react considerably faster than the _cis_ isomers. The optimum conditions for conjugation are generally present in _trans_ 1, 2-diarylcyclopropanes. In the _cis_ isomers on the other hand, all confor-

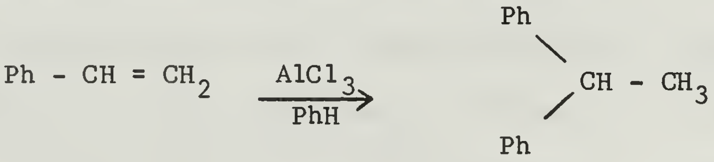




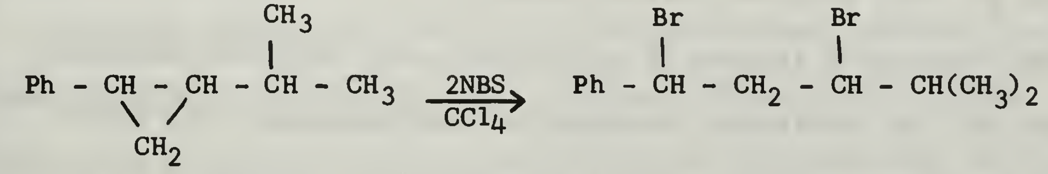
mations are not possible and the extent of pi orbital overlap for conjugation is not as great. Numerous examples of the increased reactivity of conjugated cyclopropanes as compared to non-conjugated cyclopropanes have been observed. A comprehensive review of the hydrogenation of alkyl- and aryl-cyclopropanes has been prepared by Lukina (90).

Other studies have been carried out which emphasize the similarity between cyclopropanes and alkenes. Alkylation studies using phenycyclopropane and para substituted phenycyclopropanes have been carried out in benzene using aluminum chloride (61). The cyclopropanes were shown to react without prior isomerization in yields of 52-72% giving the 1, 1-diphenylpropanes. The reaction of styrene and its para substituted analogs are similar giving the 1, 1-diphenylethane.



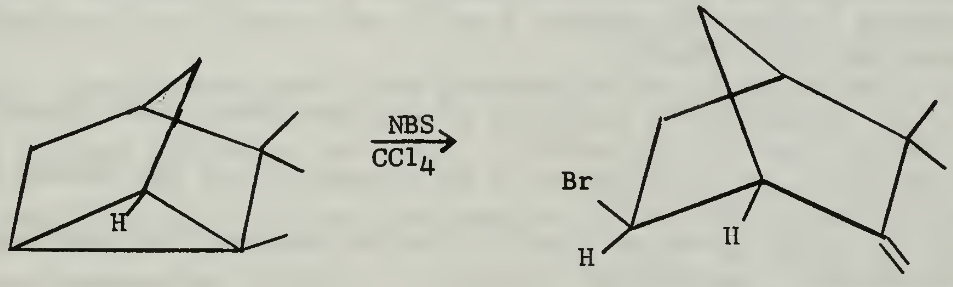


Some cyclopropane derivatives have been reported (36) to exhibit low reactivity toward free radicals. Cyclopropylcyanide, methyl cyclopropyl ketone, and phenylcyclopropane were found to be unreactive in attempts at radical propagated polymerizations. The olefinic analogs of these cyclopropanes readily undergo polymerization under the same reaction conditions. Kuivila *et al.*(56) examined the reactivity of 1-phenyl-2-ethylcyclopropane and 1-phenyl-2-isopropylcyclopropane XVIII with N-bromosuccinimide. No reaction was observed unless benzoyl peroxide was present.



XVIII XIX

In the presence of benzoyl peroxide a dibromide(XIX) was obtained. A similar reaction has been observed with tricyclene (XX) in an attempt to produce allylic bromination in cyclopropanes as in alkenes.



XX

Other addition reactions which are sometimes used to identify olefins fail for cyclopropanes. Substituted cyclopropanes generally fail to react with ozone or react with considerable difficulty. Alkenes readily react to form ozonides. Alkenes react readily with dilute potassium permanganate to form *alpha*,*beta*-diols. Cyclopropanes fail to react with dilute potassium permanganate. This fact has been used to rid cyclopropanes of unwanted olefinic impurities (48).

In addition to the reactions cited above which have been the classic criteria for unsaturation, cyclopropanes exhibit spectral features which indicate unsaturation. The infrared carbon-hydrogen stretch absorption of cyclopropane lies above 3000 cm^{-1}, whereas alkenes also have carbon-hydrogen stretch frequencies above 3000 cm^{-1}. In contrast cyclobutane and higher numbered cyclic alkanes have carbon hydrogen stretch frequencies at lower energies, below 3000 cm^{-1}.

The ultraviolet spectra of arylcyclopropanes provides additional evidence for the unsaturated character of cyclopropanes. The bathochromic shift observed for carbonyl compounds when conjugated is also observed for carbonyl compounds with a cyclopropyl group spanning the *alpha*,*beta* position. Similar shifts are observed when comparing the ultraviolet absorption of ethyl benzene, phenylcyclopropane and styrene. Phenylcyclopropane is found to absorb at a value intermediate between styrene and ethyl benzene.

This review of the synthesis of cyclopropanes, their properties and reactions was not intended to be exhaustive and the reader is referred to review articles cited in the bibliography for more comprehensive discussions.

EXPERIMENTAL PART I

Preparation of the Isomeric 1,2-Diarylcyclopropanes

All of the cyclopropanes were prepared by either (1) the thermal decomposition of the appropriate 3, 5-diaryl-1-pyrazoline or (2) the base pyrolysis of the 3, 5-diaryl-2-pyrazoline. The 3, 5-diaryl-1-pyrazolines were prepared by the addition of the appropriately para-substituted phenyldiazomethanes to styrene. The 3, 5-diaryl-2-pyrazolines were prepared by the addition of hydrazine to the appropriate 1, 3-diarylpropenone.

Infrared spectra were recorded on a Perkin-Elmer Infrared Spectrograph Model 621. All liquids were done neat between Cesium Iodide discs using a 0.015 mm spacer. KBr pellets or 20% solutions in CCl_4 or CS_2 were used for solids as indicated. NMR spectra (given in ppm delta) were recorded as given in Appendix II.

Ultraviolet spectra were recorded on a Beckman Model DB Spectrophotometer with the exception of some of the kinetic studies which were carried out in a flow system using a Beckman Model DK-1A Spectrophotometer. Gas chromatograms were prepared on an Aerograph Hy-Fy Model 600 using a flame ionization detector. A 5 foot by 1/8 inch 5% SE-30 on 60/80 mesh Chromsorb W column was used at a flow rate of 20 cc/minute and an over temperature of 200^{o}C. Molecular weights were determined on a Mechrolab Vapor Pressure Osmometer in carbon tetrachloride.

Preparation of Phenyldiazomethane (74)

Into a 1 liter three necked round bottom flask, fitted with stirrer, dropping funnel, and reflux condenser, was placed 60 g (1.8 moles) of 95% hydrazine in 600 ml of ether. Benzaldehyde, 106 g (1.8 moles), was added over a period of fifteen minutes. After removal of the water layer produced, 300 g (1.4 moles) of mercuric oxide (red powder) was added slowly with stirring. The slurry was allowed to stir in the dark for three hours after completion of the addition of the mercuric oxide. The mixture was allowed to settle for thirty minutes, the dark red solution was decanted through an ultra-fine sintered glass filter and used without further purification.

Preparation of 3, 5-Diphenyl-1-pyrazoline

To the deep red etherealsolution of phenyldiazomethane was added 35 g (0.34 moles) of freshly distilled styrene in 90 ml of ether. The addition was carried out dropwise with stirring over a period of one hour in a 1 liter three neck flask wrapped in aluminum foil. The solution was stirred for 24 hours in the dark and then evaporated on a rotary evaporator to about one half volume. The solution (ca 250 ml) was stirred in an ice-salt bath for two and one-half hours. The precipitate formed during this time was filtered and the crystalline material washed twice with ice cold ether. The crystalline pyrazoline was recrystallized from warm methyl alcohol and dried *in vacuo*, in a desiccator, over phosphorous pentoxide to give 12 g (18% yield based on styrene) of white shiny flakes,[1] m.p. 108° dec.; 109-110°dec. (74). The ultraviolet spectrum gave a single peak, λ_{max} (ETOH) 327 mμ, ϵ_{max} 345; λ_{max} (ETOH) 329 mμ, ϵ_{max} 291 (74). The infrared spectrum (KBr pellet) showed a sharp band at 1552 cm^{-1} (105); 1548 cm^{-1} (74).

Preparation of d,l-*trans*-1, 2-Diphenylcyclopropane

The 3, 5-diphenylpyrazoline prepared above was added to 125 ml of benzene and refluxed for three hours. The benzene was removed under reduced pressure to give a colorless liquid. The pure d,l-*trans*-1, 2-

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[1] The white crystalline pyrazoline decomposed slowly to a brown oil while standing at room temperature in an open flask.

diphenylcyclopropane had the following physical constants: n_D^{25} 1.5987, n_D^{23} 1.5987 (74); b.p. 115-118° / 1 torr, 122-126° / 2 torr (52). N.M.R. (Spectrum #1, Appendix II); a multiplet centered at 2.10ppm, 2.13 ppm (20); a multiplet centered at 1.28 ppm and a multiplet centered at 7.05 ppm, 7.27 ppm (20). IR 1208, 1027, 746-732 (doublet) 695 and 515 cm^{-1} (Appendix I, Spectrum #1); 1218, 750, 735 and 695 cm^{-1} (52).

Analysis

	%C	%H
Calculated ($C_{15}H_{14}$)	92.74	7.26
Found	92.80	7.23

Attempted Preparation of 1, 2-Diphenylcyclopropane via Methylene Iodide Addition to Stilbene (93)

Several attempts were made to prepare 1, 2-diphenylcyclopropane by the addition of a divalent carbon intermediate to carbon-carbon unsaturation using an active zinc-copper couple and methylene iodide. A typical synthesis was as follows: The active zinc-copper couple (59) was prepared using 0.6 g (0.003 moles) cupric acetate dissolved in 15 ml of hot glacial acetic acid. Added to this solution was 5.4 g (0.08 moles) zinc dust while stirring rapidly. After stirring for one minute the solution was allowed to settle and the acetic acid decanted. The reddish brown couple was washed once with 20 ml glacial acetic acid and three times with 30 ml portions of ether. The couple was protected in 30 ml of ether and 5 g (0.033 moles) of cis-stilbene added. In 30 ml of ether, 16.7 g (0.06 moles) methylene iodide was added dropwise to the gently refluxing ether, stilbene, and couple mixture. The mixture was refluxed with stirring for 20 hours. Gas chromatography of the mixture on a Beckman GC-4 using a 12' by 1/8" 0.5% SE-30 on DMCS Chromsorb W column, indicated only traces of 1, 2-diphenylcyclopropane. No further attempts to use this procedure as a synthetic route for 1, 2-Diarylcyclopropanes were made.

Preparation of 3, 5-Diphenyl-2-pyrazoline

To a solution of 62 g (0.3 moles) of benzalacetophenone (54) m.p. 52°, cf. 56-58° (100), in a 1 liter round bottom flask fitted with stirrer, reflux condenser, nitrogen inlet, and dropping funnel, was added 10.5 ml (0.35 moles) of 95% hydrazine in 75 ml of 95% ethyl alcohol. The temperature was kept at 50-60°C during the three hours necessary for dropwise addition of hydrazine. A large crop of white crystals was obtained by placing the pale yellow reaction mixture in a refrigerator overnight. The mixture was filtered and the solid used immediately[1] in the following pyrolysis.

Preparation of Isomeric 1, 2-Diphenylcyclopropanes

Powdered potassium hydroxide (10 g) was mixed with the 3, 5-diphenyl-2-pyrazoline and the mixture quickly transferred to a 500 ml Florence flask fitted with nitrogen inlet and immersed in a wax bath at 150°C. At about 160°C the mixture melted and at 210°C (bath temperature) a vigorous evolution of gas occurred. The mixture was held at this temperature for fifteen minutes, cooled and taken up in ether. The ether solution was extracted three times with H_2O, dried over anhydrous K_2CO_3 and the ether evaporated. The residue was distilled through a semi-micro spinning band column giving a total of 19 g (33% yield overall) of the *cis* and dl-*trans*-1, 2-diphenylcyclopropanes. The purity of the distilled fractions was determined by g.l.c.. The dl-*trans*-1, 2-diphenylcyclopropane obtained had identical properties to those given above for dl-trans-1, 2-diphenylcyclopropane prepared from the 1-pyrazoline. cis-1, 2-Diphenylcyclopropane had the following physical constants. B.p. 73° / 0.25 torr; 126.5-129° C/3.8 torr (52). $n_D^{25°}$ 1.5925; n_D^{20} 1.5892 (52). U.V: λ_{max} 220 mμ, ϵ_{max} 1.6 X 10^4; λ_{max} 220 mμ, ϵ_{max} 1.2 X 10^4 (52) N.M.R.: multiplets centered at 2.38 ppm, 2.45 ppm (20); 1.34 ppm, and 6.95 ppm, 6.96 ppm (20). IR. 1197, 1027, 1010, 758, 730, 718, 695, and 512 cm^{-1} (Spectrum #2, Appendix I); 1204, 1017, 770, 749, and 695 cm^{-1} (52).

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[1] The 3, 5-diphenyl-2-pyrazoline decomposes rapidly when exposed to air at room temperature.

Preparation of p-Methyl-Phenyldiazomethane

In a manner similar to the preparation of phenyldiazomethane, 100 g (0.83 moles) of p-tolualdehyde in 50 ml ether was added to 50 g (1.55 moles) of 95% hydrazine in 500 ml ether. The addition was carried out dropwise with stirring over a period of one hour. In a 1 liter round bottom flask, 300 g (1.4 moles) of mercuric oxide was placed along with 100 ml ether, and the etherealsolution of the p-tolualdehyde hydrazone (after removal of the water produced) was added slowly with stirring. After stirring for four hours the mixture was filtered through an ultra fine sintered glass filter and the deep red filtrate placed in a 1 liter round bottom flask fitted with stirrer and dropping funnel and wrapped in aluminum foil. Freshly distilled styrene, 30 g (0.29 moles), in 80 ml of ether was added over a one hour period. The reaction mixture was stirred for 27 hours in the dark. The volume was reduced to approximately 200 ml on a rotary evaporator, and the mixture was then stirred in an ice bath for two hours. After filtration and washing of the small amount of white crystalline material, the filtrate was reduced in volume to approximately 100 ml and cooled in a dry ice-acetone slurry. Filtration yielded some additional 3-phenyl-5-(p-methylphenyl)-1-pyrazoline. A total of 10 g (15.5% based on styrene) was obtained after recrystallization from warm methyl alcohol, m.p. 90-91°. U.V.; λ_{max} (ETOH) 308 mμ ϵ_{max} 513; I.R.; (KBr pellet) 1550 cm^{-1} (s).

Preparation of d,l-*trans*-1-(p-Methylphenyl)-2-phenylcyclopropane

To 100 ml of benzene, 10 g of the 3-phenyl-5-(p-methylphenyl)-1-pyrazoline (prepared above) was added and heated at reflux for 2 hours. The benzene was removed under reduced pressure and the remaining light yellow liquid distilled under reduced pressure giving pure d,l-*trans*-1-(p-methylphenyl)-2-phenylcyclopropane b.p. 142-146° / 0.6 torr; n_D^{25} 1.5895.

Analysis

	%C	%H
Calculated $C_{16}H_{16}$	92.26	7.74
Found	92.30	7.79

Structural confirmation was obtained via N.M.R. (Spectrum #3, Appendix II) with multiplets centered at 1.28 ppm, 2.05 ppm and 7.00 ppm and a singlet, at 2.28 ppm. I.R. (Spectrum #3, Appendix I); 1208, 1028, 758-747 (doublet), 693, and 510 cm^{-1}. U.V.: λ_{max} (ETOH) 234 mμ, ϵ_{max} 2.19 X 10^4.

Preparation of 1-Phenyl-3-(p-methylphenyl)-propenone

To a solution of 27 g (0.7 moles) of NaOH in 500 ml of 50% ethyl alcohol, 65 g (0.54 moles) of acetophenone and 60 g (0.5 moles) of p-tolualdehyde were added rapidly with vigorous stirring. The reaction temperature was kept below 25° while stirring for one hour. After chilling the mixture in a refrigerator for two hours, it was filtered and the pale yellow crystals washed with water until neutral. Recrystallization from ethyl alcohol gave 85 g (78% yield) of the 1-(p-methylphenyl)-3-

phenylpropenone. M.p. 95-96°, 96.5° (110); I.R.; (C=O), 1680 cm^{-1}; U.V.: λ_{max} (ETOH) 325 mμ, ϵ_{max} 2.9 X 10^4; λ_{max} (ETOH) 333 mμ(1).

Preparation of 3-Phenyl-5-(p-methyl-phenyl)-2-pyrazoline

In an apparatus similar to that used for the preparation of 3, 5-diphenyl-2-pyrazoline, 44.4 g (0.2 moles) 1-phenyl-3-(p-methylphenyl)-propenone was placed in 120 ml of warm ethyl alcohol. To this was added over a period of two hours a solution of 8 g (0.25 moles) of 95% hydrazine in 50 ml of ethyl alcohol. The reaction mixture was stirred for an additional two hours, cooled and placed in a refrigerator. A large crop of white crystals was obtained on filtration and used immediately in the following pyrolysis.

Preparation of Isomeric 1-(p-Methylphenyl)-2-phenylcyclopropanes

The 2-pyrazoline was mixed with 5 g of powdered KOH and placed in a 500 ml Florence flask fitted with a nitrogen inlet. The mixture was placed in a wax bath at 225°C for fifteen minutes during which time a vigorous evolution of gas occurred. The mixture was cooled, taken up in ether, extracted three times with water and dried over anhydrous K_2CO_3. After evaporation of the ether the remaining light yellow liquid was distilled through a semi-micro spinning band column giving pure fractions of two colorless liquids. The trans isomer, b.p. 104-105° C/0.1 torr was identical (IR, U.V. and N.M.R.) to the trans isomer, produced via the thermal pyrolysis of the 1-pyrazoline. The cis isomer had the following properties: b.p. 94-95° / 0.1 torr; n_D^{25} 1.5808. N.M.R. (Spectrum #4, Appendix II); multiplets centered at 1.22 ppm, 2.22 ppm, and 6.82 ppm and a singlet at 2.05 ppm in the ratio 2:2:9:3 respectively. IR (Spectrum #4, Appendix I); 1375-1360 (doublet), 1194, 1028, 763, 720, 693 and 509 cm^{-1}. U.V. λ_{max} 223 (s) mμ, ϵ_{max} 1.78 X 10^4.

Preparation of p-Chlorophenyldiazomethane

In a 1 liter flask fitted with stirrer and condenser was placed 60 g (1.78 moles) of 95% hydrazine and 400 ml of ether. To this was added, at a rate sufficient to keep the ether at reflux, 140 g (1.0 moles) of p-chlorobenzaldehyde. After stirring for an additional hour the reaction mixture was allowed to settle and the water layer produced was removed. This ethereal solution of the hydrazone was added slowly, with stirring, to a mixture of 100 ml of ether and 300 g (1.4 moles) of mercuric oxide in a 1 liter round bottom flask. The mixture was stirred overnight and then allowed to settle for one hour. The dark red solution was decanted through an ultra-fine sintered glass filter and used below.

Attempted Preparation of 3-(p-Chlorophenyl)-5-phenyl-1-pyrazoline

The deep red ethereal solution of p-chlorophenyldiazomethane was placed in a 1 liter round bottom flask fitted with stirrer, dropping funnel and condenser and wrapped in aluminum foil. Freshly distilled styrene, 40 g (0.38 moles) in 100 ml of ether, was added dropwise and the reaction mixture stirred in the dark for 22 hours. The volume was reduced to approximately 250 ml and the mixture stirred in an ice bath for one hour. Filtration yielded a small amount of a gray-white crystalline material which decomposed rapidly to produce a yellow material. The yellow material obtained failed to undergo pyrolysis with the generation of nitrogen in refluxing benzene. Two additional attempts were made to obtain this pyrazoline by this method but both were also unsuccessful.

Preparation of 1-(p-Chlorophenyl)-3-phenylpropenone

In a 2 liter round bottom flask fitted with stirrer, was placed 54 g (1.35 moles) NaOH in 300 ml ethyl alcohol and 130 g (1.08 moles) acetophenone. Rapid stirring was started and 150 g (1.07 moles) of p-chlorobenzaldehyde (crushed to a fine powder) was added quickly. The temperature was kept below 30°C for the first half hour then lowered to 15°C where stirring was continued for three hours. The mixture was placed in a refrigerator for four hours whereupon a large crop of dirty yellow crystals were obtained. After filtration and washing with H_2O until neutral the crystals were dried in an oven at 100°C. A total of 240 g (93% yield) of material was obtained which had the following properties. M.p. 112.5-113.5, $114-115^{\circ}$C (100). IR, (C=O), 1681 cm^{-1}. U.V.: λ_{max} (ETOH) 315 mμ, λ_{max} (ETOH) 314 mμ (100).

Preparation of 3-(p-Chlorophenyl)-5-phenyl-2-pyrazoline

In an apparatus similar to that used for the preparation of 3, 5-diphenyl-2-pyrazoline, 46.6 g (0.19 moles) of 1-phenyl-3-(p-chlorophenyl) propenone in 120 ml of ethyl alcohol was placed. Added to this, dropwise, over a period of two hours was a solution of 8 g (0.25 moles) of hydrazine in 50 ml ethyl alcohol. The temperature of the reaction mixture was kept between $50-60^{\circ}$C throughout. A white precipitate appeared after one hour. The flask was stoppered and placed in a refrigerator for three hours. Filtration yielded a pure white crystalline material which was used immediately in the following synthesis.[1]

Preparation of Isomeric 1-(p-Chlorophenyl)-2-phenylcyclopropane

The pure white pyrazoline (above) was ground up immediately with 8 g of powdered KOH, placed in a 500 ml Florence flask fitted with a nitrogen inlet and placed in a wax bath. At $150-160^{\circ}$C (bath temperature) the mixture melted. At 210°C (bath temperature) a vigorous evolution of gas was observed. The reaction mixture was kept at 220°C for one half hour. After cooling, the liquid mixture was taken up in ether and extracted three times with water. The ether was removed and the liquid distilled through a semi-micro spinning band column under reduced pressure giving a total of 24 g (42%) in two (cis and trans) fractions having the following properties. cis-n_D^{25} 1.5951. N.M.R. (Spectrum #5, Appendix II); multiplets at 1.30 ppm, 2.32 ppm, and 6.95 ppm in the ratio 2:2:9 respectively. IR, (Spectrum #5, Appendix I); 1370-1360 (doublet), 1194, 1027, 767, 714, 694 and 521 cm^{-1}. U.V.: λ_{max} (ETOH) 225 mμ, ϵ_{max} 1.55 X 10^4. Trans isomer n_D^{25} 1.6066. N.M.R. (Spectrum #6, Appendix II); multiplets centered at 1.30 ppm, 2.11 ppm, and 7.09 ppm in the ratio 2:2:9 respectively. IR, (Spectrum #6, Appendix I); 1207, 1027, 772, 742, 693, and 518 cm^{-1}. U.V. λ_{max} (ETOH) 236 mμ, ϵ_{max} 2.58 X 10^4.

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[1] A small amount of the white crystalline material was dissolved in CCl_4 and an infrared spectrum run. The solution became yellow after one-half hour and dark brown after two hours. The spectrum was very similar to that obtained for 3, 5-diphenyl-1-pyrazoline with a sharp band at 1550 cm^{-1}. The U.V. Spectrum gave two absorption peaks at 293 mμ and 220 mμ. Attempts to dry some of this material in vacuo in a desiccator over P_2O_5 gave only a brown decomposition product, which could not be identified.

Analysis

	%C	%H	%Cl
Calculated $C_{15}H_{13}Cl$	78.79	5.70	15.50
Found	78.98	5.70	15.32

Preparation of 1-Phenyl-3-(m-chlorophenyl)-propenone

In a 0.5 liter round bottom flask fitted with stirrer was placed 25 g (0.18 moles) of m-chlorobenzaldehyde, 22 g (0.18 moles) of acetophenone, 1 ml of a 50% NaOH solution and 100 ml of ethyl alcohol. The mixture was stirred at room temperature for two hours and placed in a refrigerator overnight. The pale yellow precipitate was filtered off, washed once with ice cold ethyl alcohol and used without further purification.

Preparation of 3-phenyl-5-(m-chlorophenyl)-2-pyrazoline

Using a procedure similar to that used for the preparation of the 3-phenyl-5-(p-chlorophenyl)-2-pyrazoline this pyrazoline was prepared. Pure white crystals were obtained which were used immediately in the following synthesis.

Preparation of Isomeric 1-(m-Chlorophenyl)-2-phenylcyclopropanes

The pyrazoline was ground up with 0.1 g of powdered KOH, placed in a Florence flask fitted with nitrogen inlet and lowered into a wax bath at 220°C. Evolution of gas began almost immediately. The mixture was kept at this temperature for ten minutes, cooled, transferred to a distillation pot and distilled through a semi-micro spinning band. The distillate was taken in three fractions giving a total of 19 g (44% yield overall based on 3-chlorobenzaldehyde). Fraction I (cis isomer) showed only one component on g.l.c. and had the following properties. B.p. 96-98° / 0.5 torr, n_D^{25} 1.5925. N.M.R. (Spectrum #7, Appendix II); multiplets at 1.37 ppm, 2.40 ppm, and 6.92 ppm in the ratio 2:2:9. IR, (Spectrum #7, Appendix I); 1372-1355 (doublet), 1194, 1025, 761, 717, 695 and 517 cm^{-1}. U.V.: λ_{max} (ETOH) 216 mμ ϵ_{max} 1.94 X 10^4.

Analysis

	%C	%H	%Cl
Calculated $C_{15}H_{13}Cl$	78.79	5.70	15.50
Found	78.85	5.67	15.48

Fraction II showed two components on g.l.c. (Approximately equal mixture of fractions I and III). Fraction III (trans isomer) had the following properties. n_D^{25} 1.6062. N.M.R.; multiplets centered at 1.28 ppm, 2.00 ppm and 7.08 ppm, in the ratio 2:2:9 respectively. IR, (Spectrum #8, Appendix I); 1207, 1028, 776, 742, 693, and 502 cm^{-1}. U.V.; λ_{max}

(ETOH) 233 $m\mu$, ϵ_{max} 2.28 X 10^4.

Preparation of 1-Phenyl-3-(p-fluorophenyl)-propenone

In a 0.5 liter round bottom flask fitted with stirrer was placed 32.5 g (0.27 moles) of acetophenone, 30 g of p-fluorobenzaldehyde, 250 ml ethyl alcohol and 0.5 g NaOH. The mixture was stirred for one hour while keeping the temperature below 25°C. After refrigeration for two hours, pale yellow crystals appeared which were filtered from the reaction mixture, washed three times with water and dried. Nearly a quantitative yield was obtained for the product. M.p. 80-83°C. I.R.: ($C=O$) 1683 cm^{-1}. U.V.; λ_{max} (ETOH) 313 $m\mu$, ϵ_{max} 2.59 X 10^4.

Preparation of 3-Phenyl-5-(p-fluorophenyl)-2-pyrazoline

To an alcoholic solution of the above propenone, 8 g (0.25 moles) of hydrazine in 50 ml of ethyl alcohol was added dropwise over a period of one hour at 50-60°C. As with the preparation of previous 2-pyrazolines the reaction was carried out under a nitrogen atmosphere and stirring was continued for an additional hour after the addition of the hydrazine. After refrigeration of the reaction mixture for two hours a large crop of pure white crystals were obtained which were filtered and used immediately in the following pyrolysis.

Preparation of Isomeric 1-(p-Fluorophenyl)-2-phenylcyclopropane

Following filtration of the above precipitate the crystals were ground together with 0.5 g of powdered KOH and placed in a 0.5 liter Florence flask and placed in a wax bath. Pyrolysis took place at 210°C (bath temperature) with a vigorous evolution of gas. After cooling, the liquid was taken up in ether, extracted three times with water and dried over anhydrous K_2CO_3. Removal of the ether under reduced pressure and distillation of the remaining pale yellow liquid through a semi-micro spinning band column gave two fractions. Each fraction contained only a single component as shown by g.l.c. Fraction I (cis isomer) had the following properties. B.p. 125°C / 1.3 torr. n_D^{25} 1.5655. N.M.R. (Spectrum #9, Appendix II), multiplets centered at 1.30 ppm, 2.31 ppm and 6.90 ppm in the ratio 2:2:9 respectively and a multiplet centered at 117.9 ppm relative to $CFCL_3$. IR; (Spectrum #9, Appendix I); 1370 (s), 1360, 1193, 1024, 763, 720, 691 and 510 cm^{-1}. U.V. λ_{max} (ETOH) 220 mμ, ϵ_{max} 1.46 X 10^4. Lit. values (89) b.p. 136.5° / 8 torr, n_D^{20} 1.5664.

Analysis

	%C	%H	%F
Calculated $C_{15}H_{13}F$	84.91	6.11	8.98
Found	84.91	6.13	8.69

Fraction II (trans isomer) had the following properties. B.p. 130° C / 1.3 torr. n_D^{25} 1.5779. N.M.R. (Spectrum #10, Appendix II); multiplets centered at 1.30 ppm, 2.00 ppm, and 7.00 ppm in the ratio 2:2:9 respectively and a multiplet centered at 118.4 ppm relative to $CFCl_3$. IR, (Spectrum #10, Appendix I); 1203, 1027, 860-847 (doublet), 691 and 514 cm^{-1}. U.V. λ_{max} (ETOH) 230 mμ, ϵ_{max} 1.73 X 10^4. Lit. values (89) b.p. 172-173° / 15 torr, n_D^{20} 1.5743.

Preparation of p-Methoxyphenyldiazomethane

Anisaldehyde, 136 g (1.0 moles), was dissolved in 500 ml ether and placed in a 1 liter three necked round bottom flask fitted with stirrer, condenser, and dropping funnel. To this solution 66 g (2.06 moles) of anhydrous hydrazine (95) was added rapidly with stirring. The water layer produced was quickly removed in a separatory funnel and the ethereal hydrazone solution added slowly with stirring to a slurry of 100 ml ether and 300 g (1.4 moles) of mercuric oxide (red powder). The mixture was stirred for one hour then allowed to settle for one half hour before the deep red ethereal solution was decanted through an ultra fine sintered glass filter.

Preparation of 3-Phenyl-5-(p-methoxyphenyl)-1-pyrazoline

To the ethereal diazo solution in a 1 liter round bottom flask wrapped in aluminum foil, 36 g (0.34 moles) of freshly distilled styrene in 90 ml of ether was added. The addition was carried out in the dark over a 45 minute period. Stirring was continued for thirty-six hours in the dark. At the end of this time the reaction mixture was light orange in color with some yellow solid in the flask. The yellow solid was filtered off and the filtrate reduced in volume to about 200 ml on a rotary evaporator. Additional yellow precipitate appeared and was filtered off. Further evaporation followed by stirring in an ice bath for two hours produced a small amount of white precipitate in the flask. The precipitate[1] was used immediately in the following pyrolysis.

Preparation of d,l-trans-1-(p-Methoxyphenyl)-2-phenylcyclopropane

The crude precipitate was placed in 200 ml of benzene and heated to reflux. The evolved gases were trapped and analyzed on a Fisher-Hamilton Gas Partitioner. Results indicated about 0.032 moles of nitrogen had been given off. After cooling, the benzene was removed under aspirator pressure and the remaining pale yellow liquid distilled under reduced pressure. Three nearly colorless fractions, which solidified in the receivers, were taken. Three recrystallizations from ethyl alcohol gave 6 g (0.025 moles) (7% based on styrene) of a pure white solid, m.p. 78.5-79.5. M.W.[2] 223 (theoretical 224.1). N.M.R. (Spectrum #11, Appendix II); multiplets centered at 1.32 ppm, 2.10 ppm and 7.0 ppm, and a singlet at 3.75 ppm in the ratio 2:2:9:3 respectively. IR, (KBr pellet, Spectrum #11, Appendix I); 1205, 1023 (shoulder), 760, 740, 702 and 513 cm^{-1}. U.V. λ_{max} (ETOH) 232 mμ, ϵ_{max} 1.98 X 10^4.

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[1] Exposure to air at room temperature caused decomposition immediately to a yellow-brown oil.

[2] Determined on a vapor pressure osmometer in CCl_4.

Analysis

	%C	%H
Calculated $C_{16}H_{16}O$	85.19	7.13
Found	85.66	7.20

Preparation of 1-Phenyl-3-(p-methoxyphenyl)-propenone

In a 1 liter round bottom flask fitted with stirrer was placed 65 g (0.54 moles) of acetophenone in 500 ml of a 50% ethyl alcohol solution. Stirring was begun with cooling in an ice bath as 27 g (0.68 moles) NaOH was added. This was followed immediately by the addition of 75 g (0.54 moles) of anisaldehyde. The temperature was kept below 25°C while stirring for 1.5 hours. The light yellow solution was placed in a refrigerator overnight whereupon a large crop of light yellow crystals were obtained. The mixture was filtered and the crystalline material washed with water until the wash was neutral. Recrystallization from ethyl alcohol gave 83 g (65% yield) of pale yellow crystals. M.p. 77-78°C; 79°C (78).

Preparation of 3-Phenyl-5-(p-methoxyphenyl)-2-pyrazoline

In a 1 liter round bottom flask fitted with stirrer, reflux condenser, dropping funnel, and nitrogen inlet was placed 84 g (0.35 moles) of 1-phenyl-3-(p-methoxyphenyl)-propenone in 240 ml of ethyl alcohol. The mixture was heated to 50°C and 17 g (0.5 moles) of 95% hydrazine in 100 ml of ethyl alcohol was added dropwise over a three hour period. Stirring was continued for an additional 8 hours while the temperature was maintained at 60-70°C. After refrigeration of the solution for two hours a heavy white precipitate was obtained. The reaction mixture was filtered, the crystalline precipitate washed with ice cold ether and pressed dry with a rubber dam.

Preparation of Isomeric 1-(p-Methoxyphenyl)-2-phenylcyclopropanes

Without further purification the above pyrazoline was transferred quickly to a Florence flask fitted with a nitrogen inlet and placed in a wax bath. The bath was heated to 260°C but no noticeable pyrolysis occurred. After cooling to below 200°C a trace of powdered KOH was added to the flask and heating started anew. At 215°C a vigorous evolution of gas took place. The yellow-brown liquid was cooled, extracted once with water, dried over anhydrous K_2CO_3 and the ether evaporated in a vacuum over at 40°C. A light yellow mushy solid was obtained which was recrystallized from ethyl alcohol twice, giving a good yield of pure white crystals which were identical in all respects to the d, 1-*trans* 1-(p-methoxyphenyl)-2-phenylcyclopropane prepared previously. The mother liquors were combined and the ethyl alcohol and water removed in a vacuum oven at 60°C. Approximately 2 g of a pale yellow liquid was obtained. Distillation gave 1 g of the pure *cis* compound. B.p. 141° / 0.45 torr; n_D^{25} 1.5885. N.M.R. (Spectrum #12, Appendix II); multiplets centered at 1.28 ppm., 2.31 ppm, and 6.78 ppm and a singlet at 3.45 ppm in the ratio 2:2:9:3. IR, (Spectrum #12, Appendix I); 1360, 1196, 1028 (shoulder), 767, 727 and 694 cm^{-1}. U.V. λ_{max} 229 mμ , ϵ_{max} 1.14×10^4.

Attempted Preparation of Isomeric 1-(p-Nitrophenyl)-2-phenylcyclopropane

Several attempts were made to prepare this substituted cyclopropane by preparation of the p-nitrophenyldiazomethane. Oxidation of the p-nitrobenzalhydrazone with mercuric oxide yielded only intractable tars.

Attempted Preparation of dl-*trans*-1-(m-Nitrophenyl)-2-phenylcyclopropane

Phenyldiazomethane was prepared as above. To this dry red ethereal solution 8 g (0.06 moles) of m-nitrostyrene in 50 ml of ether was added dropwise with stirring. After the addition was complete (*ca.* one hour) the mixture was stirred overnight in the dark. This solution was divided into two equal portions. One portion was evaporated by one half and stirred in an ice bath for two hours. Filtration yielded a small amount of a pale yellow crystalline material. This was placed immediately in refluxing benzene. No evolution of gas occurred. A small portion of the benzene solution was evaporated and then taken up in CCl_4. An IR spectrum of the CCl_4 solution indicated that none of the desired cyclopropane was present.

The second half of the phenyl-diazomethane and m-nitrostyrene solution was stirred for a total of 72 hours in the dark. This solution was then placed in a refrigerator for two weeks. Some pale orange-white crystals were obtained on filtration. These crystals were placed in benzene and brought to reflux rapidly. A gas trap indicated that 180 ml of gas had been evolved. Work up of the benzene solution gave 0.05 gms of a white crystalline material. The ultraviolet and infrared spectrum were inconclusive in establishing the identity of this product.

Additional phenyldiazomethane was prepared and added to an etheral solution of m-nitrostyrene. This solution was photolyzed for three hours in a quartz cell with a mercury vapor lamp. No identifiable products were obtained on work up.

Preparation of 1-(p-Nitrophenyl)-3-phenylpropenone

In a 1 liter round bottom flask fitted with a stirrer was placed 55 g (0.33 moles) of p-nitroacetophenone in 150 ml of ethyl alcohol.

Ten drops of a 50% NaOH solution was added followed by 30 g (0.33 moles) of benzaldehyde. The mixture was stirred at room temperature for one and one-half hours, after which time a thick reddish-brown paste had formed. The mixture was filtered and washed three times with water. Recrystallization from ethyl alcohol gave 50 g (60% yield) of a pale yellow solid. M.p. 146°C; 146.5°C (100)

Attempted Preparation of Isomeric 1-(p-Nitrophenyl)-2-phenylcyclopropane

To a solution of 27 g (0.09 moles) of 1-(p-nitrophenyl)-3-phenylpropenone in 120 ml of ethyl alcohol was added 20 g (0.62 moles) of 95% hydrazine. The addition was carried out dropwise with stirring over a period of 2 hours while the temperature was maintained between 60°C and 65°C. After chilling in a refrigerator for one hour the mixture was filtered to give a good yield of orange-yellow crystals. These crystals were ground immediately with 1 g of powdered KOH and heated in a wax bath to 225°C (bath temperature). Only a dark brown tar was obtained from which no identifiable products were obtained. Further attempts to prepare any of the nitro substituted diarylcyclopropanes were not made.

Preparation of 1-Phenyl-3-(p-dimethyaminophenyl)-propenone

To a solution of 60 g (0.5 moles) of acetophenone and 0.5 g NaOH in 180 ml of ethyl alcohol was added rapidly, with vigorous stirring, 75 g (0.5 moles) of p-dimethylaminobenzaldehyde. The mixture was stirred at room temperature for seven hours whereupon a dark brown oil layer separated. After separation of the water layer, the mixture was placed in a refrigerator. The oil layer solidified after ten days to a yellow-brown mass. The solid was filtered off and washed with water three times. Recrystallization from ethyl alcohol gave bright orange-yellow crystals. M.p. 105°C, 113-114°C (87); U.V. λ_{max} (ETOH) 264 mμ , ϵ_{max} 2.53 X 10^4.

Preparation of 3-(p-Dimethylamino)-5-phenyl-2-pyrazoline

In an apparatus similar to that used for the preparation of 3, 5-diphenyl-2-pyrazoline, 75 g (0.31 moles) of 1-phenyl-3-(p-dimethylamino-phenyl) propenone was placed. Added to this, dropwise, over a period of one hour was a solution of 20 g (0.62 moles) of 95% hydrazine in 30 ml of ethyl alcohol. Reaction temperature was maintained between 50°C and 60°C throughout. A white precipitate appeared after one-half hour. Stirring was continued for a total of two hours and the mixture placed in a refrigerator for two hours. The mixture was filtered, the solid washed three times with ice cold ethyl alcohol, pressed dry with a rubber dam and used immediately in the following pyrolysis.

Preparation of Isomeric 1-(p-Dimethylamino)-2-phenylcyclopropane

The crystals were ground immediately with 0.05 g of powdered KOH and placed in a 0.5 l Florence flask fitted with nitrogen inlet and placed in a wax bath. At 215°C (bath temperature) a vigorous evolution of gas occurred. The mixture was cooled, taken up in ether, extracted three times with water and then dried over anhydrous K_2CO_3. After evaporation of the ether, the pale yellow liquid was distilled through an 18 inch semi-micro spinning band column and collected in seven fractions over a range from 145°C to 147°C at 0.2 torr. A total of 40 g (55% yield overall) was collected. All fractions gave only a single peak on g.p.c. analysis at 220°C.

Analysis

	%C	%H
Calculated ($C_{17}H_{19}N$)	86.03	8.07
Found	85.95	8.16

IR, (Spectrum #13, Appendix I); 1210, 993, 845 and 692 cm^{-1}. n_D^{25} 1.6140. N.M.R. (Spectrum #13, Appendix II); multiplets centered at 1.28 ppm, 2.03 ppm, and 7.10 ppm, and a singlet at 2.76 ppm.[1]

Preparation of Isomeric 1, 3-Diphenylpropenes

In a 500 ml round bottom flask fitted with stirrer, reflux condenser, and dropping funnel, 5 g of $LiAlH_4$ was placed along with 150 ml of anhydrous ether. A solution of 30 g (0.14 moles) of 1,3-diphenylacetone in 150 ml of anhydrous ether was added dropwise at a rate sufficient to keep the solution at a gentle reflux. After completion of the addition, stirring was continued for an additional thirty minutes. Water was added dropwise until the excess $LiAlH_4$ was consumed. The reaction mixture was cooled and 100 ml of 6 N HCl was added slowly with stirring. The mixture separated into two layers, a clear ether layer and a viscous, milky white water layer. Stirring was continued at room temperature for one hour after which time two layers were obtained. The ether layer was drawn off, extracted three times with water and dried over anhydrous K_2CO_3. The ethereal solution evaporated in vacuo leaving a pale yellow liquid which was used without further purification.[2]

This reduction product was transferred to a 250 ml round bottom flask and was distilled under reduced pressure (approximately 2 torr) through an 18 inch alumina packed column (66,77). The column temperature was maintained at 330°C by means of a vertical tube furnace. A total of 25 g of a pale yellow liquid was obtained which showed no infrared OH absorption.[1] This crude product was distilled through a semimicro spinning band column and taken in nine fractions, 21 g total (78% overall). Gas phase chromatography at 250°C indicated a separation into two products which were confirmed to be cis and trans-1, 3-diphenylpropene. The cis isomer, b.p. 73-75° / 0.09 torr, n_D^{25} 1.5940 had the following properties. N.M.R. (Spectrum #14, Appendix II); a doublet centered at 3.6 ppm, multiplets centered at 5.78 ppm, and 6.51 ppm and a doublet centered at 7.17 ppm in the ratio 2:1:1:10 respectively. IR, (Spectrum #14, Appendix I); 2896, 2840, 1641 (weak), 865 and 835 cm^{-1}. U.V. λ_{max} (ETOH) 243 mμ, ϵ_{max} 1.65 X 10^4.

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[1] The N.M.R. showed also a 15% impurity which appears to have the proper chemical shifts for the cis-isomer, Multiplets at 1.30 ppm, 2.30 ppm, and 6.55 ppm, and a singlet at 2.69 ppm.

[2] An infrared spectrum on this crude reduction product gave a broad OH band and the complete absence of any carbonyl absorption.

Analysis

	%C	%H
Calculated ($C_{15}H_{14}$)	92.74	7.26
Found	92.85	7.36

The trans-isomer b.p. 85° / 0.15 torr. n_D^{25} 1.5996, n_D^{20} 1.5995 (86). N.M.R. (Spectrum #15, Appendix II); multiplets centered at 3.4 ppm, 6.12 ppm, 6.39 ppm, and a singlet at 7.13 ppm in the ratio 2:1:1:10 respectively. IR, (Spectrum #15, Appendix I); 2992, 2827, 1645 (weak), 960 and 832 cm^{-1} (broad). U.V.: λ_{max} (ETOH) 250 mμ, ϵ_{max} 2.16 X 10^4, λ_{max} (ETOH) 252 mμ, ϵ_{max} 2.14 X 10^4 (76).

Analysis

	%C	%H
Calculated ($C_{15}H_{14}$)	92.74	7.26
Found	92.93	7.15

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[1] Previous attempts to dehydrate this alcohol by (1) distillation from catalytic amounts of mineral acid, (2) distillation from solid KOH, and (3) low temperature dehydration using P_2O_5 gave only partial dehydration.

Preparation of 1, 2-dibromo-1, 3-diphenylpropane

To a solution of 1 g (0.005 moles) of trans-1, 3-diphenylpropene in 10 ml of CCl_4 was added 0.05 moles bromine in CCl_4 until the color persisted for thirty minutes. The mixture was evaporated to dryness and the resulting solid dissolved in hot benzene. The benzene solution was cooled in a refrigerator whereupon a white precipitate formed. Recrystallization two more times from benzene gave pure white crystals. M.p. 105-107°, 111-112° (8). IR, (Spectrum #16, Appendix I); 2915, 2838, 590, 560 and 510 cm^{-1}. N.M.R. (Spectrum #16, Appendix II); multiplets centered at 3.18, 3.83, 4.59 and 5.00 ppm and a doublet (unsym) centered at 7.23 ppm.

EXPERIMENTAL PART II

Dark Reactions of *cis*-and *trans*-1,2-Diarylcyclopropanes with Bromine in Carbon Tetrachloride

The following procedure was used to determine the extent, if any, of reactions between bromine and the above cyclopropanes. The cyclopropane was weighed into a 100 ml volumetric flask to give a solution that was approximately 0.01 molar. Bromine from a standardized carbon tetrachloride solution was added from a microburet (to give equi-molar amounts of bromine and cyclopropane) and the flask then filled to the mark with CCl_4. The addition was carried out in total darkness with the exception of a small pen light which was used as necessary. After thoroughly mixing the solution a 5 ml aliquot was removed for determination of the initial bromine concentration and the flask then placed in a light tight cabinet at room temperature. The absorbance of the solution was measured in a 1 cm pyrex cell at 570 mμ, 550 mμ and 530 mμ (Bromine ϵ_{570} 14.0, ϵ_{550} 27.0, ϵ_{530} 48.0). Measurements were made on the initial aliquot and at 24 and 48 hours. All of the 1,2-diarylcyclopropanes prepared above were treated in this manner. Two of these compounds reacted on contact with the bromine in carbon tetrachloride solution. Both isomers of 1-(p-methylphenyl)-2 phenylcyclopropane reacted with the evolution of HBr.[1] The mixture of *cis*-and *trans*-1-(p-dimethylaminophenyl)-2-phenylcyclopropane also reacted with bromine in carbon tetrachloride to give a red-brown precipitate. This precipitate was not identified and no further reaction studies were done on this cyclopropane. Also tested in this manner along with the cyclopropanes were the cis and trans isomers of 1,3-diphenylpropene. The results of this reaction along with the remaining five isomeric cyclopropanes are summarized in the Table I below. The compounds are listed by their substituent in the structure below.

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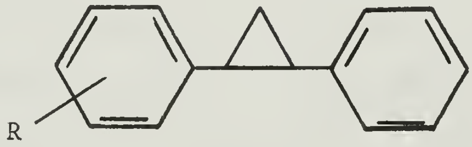
[1] Presumably this reacts in a manner similar to the bromination of toluene in non polar solvents to give benzylic bromine products. No additional work was done using this compound in the kinetic studies that follow for this reason.



Compound	Isomer	Initial Concentration(a)		After 24 hrs. Concentration(a)		After 48 hrs. Concentration(a)		Percent Reacted
R=		Cmpd	(c) Bromine	(b) Cmpd	(c) Bromine	(b) Cmpd	(c) Bromine	after 24 hrs.
para-H	cis	35.6	10.6	35.1	10.5	35.1	10.5	<1.0
	trans	21.6	10.6	21.6	10.6	21.6	10.6	0.0
para-Cl	cis	14.4	10.6	14.4	10.6	14.4	10.6	0.0
	trans	14.4	10.6	14.4	10.6	14.4	10.6	0.0
meta-Cl	cis	12.2	10.6	12.2	10.6	12.2	10.6	0.0
	trans	8.2	10.6	8.2	10.6	8.2	10.6	0.0
para-F	cis	15.2	10.6	15.2	10.6	15.2	10.6	0.0
	trans	18.0	10.6	18.0	10.6	18.0	10.6	0.0

(a), (b), (c) See Table 1b

Table I(a)

Compound	Isomer	Initial Concentration(a)		After 24 hrs. Concentration(a)		After 48 hrs. Concentration(a)		Percent Reacted
R=		Cmpd	(c) Bromine	(b) Cmpd	(c) Bromine	(b) Cmpd	(c) Bromine	after 24 hrs.
para-CH_3-O-	cis	27.2	10.6	20.6	4.6	19.5	2.90	57.0
	trans	5.6	10.6	4.9	9.9	4.3	9.3	<12.5
ϕ-CH=CH-CH_2-ϕ	cis	41.6	10.6	31.0	0.0	31.0	0.0	100.0
	trans	19.6	10.6	9.0	0.0	9.0	0.0	100.0
Control	---	----	10.6	---	10.6	---	10.6	----

(a) Millimoles per liter

(b) Based on bromine consumed

(c) Based on average values from those obtained at 570 mμ, 550 mμ, and 530 mμ.

Table I(b)

EXPERIMENTAL PART III

Photolytic Reactions of 1, 2-Diarylcyclopropanes with Bromine in Carbon Tetrachloride

Only the five isomeric 1, 2-diarylcyclopropanes listed above in Experimental Part II, Table I that underwent negligible reactions in the dark were used in these studies.

Reactions of cis-and trans-1, 2-diphenylcyclopropane

Initially, qualitative reactions of cis-and trans-1,2-diphenylcyclopropane with bromine in CCl_4 were carried out at room temperature and under existing room light (fluorescent lamps). A typical experiment was as follows: a carbon tetrachloride solution of trans-1, 2-diphenylcyclopropane was prepared by weighing 0.250 g into a 25 ml volumetric flask and adding several ml of CCl_4. Sufficient standard Br_2 in CCl_4 was added to give equal molar amounts of bromine and the cyclopropane. The flask was then diluted to the mark, stoppered and allowed to stand for approximately twenty-four hours. At the end of this time the solution was nearly colorless. Iodometric determination for bromine indicated no Br_2 remained.

Attempts were made to analyze this reaction mixture via GPC using the following columns and conditions. On an Aerograph Hy-Fy Model 600 with flame ionization detector three different columns were used isothermally under the given conditions: (1) 5' X 1/8" 5% SE-30 on DMCS 60/80 mesh at flow rates between 15 and 25 ml/min and from 150 to 250°C.; (2) A 10' X 1/8" QF-1 on DMCS 60/80 mesh at 20 ml/min and 200°C.; (3) A 10' X 1/8" carbowax 20M on DMCS 60/80 mesh at 20 ml/min and 175°C. Using a Perkin-Elmer Model 154 Vaporfractometer a 6' X 1/4" 15% polypropyleneglycol on fire brick and a 6' X 1/4" uncoated firebrick column were used.

A Beckman Model GC-4 with flame ionization detectors was also used. A 12' X 1/8" 0.5% SE-30 on Chromsorb W column was used with the temperature programmed at 5°C/minute from 100° to 250°C. In general, no well defined chromatograms from which any product identification could be ascertained were obtained.

A larger scale reaction was carried out using 0.989 g (5.92 mmol) of cis-1,2-diphenylcyclopropane in a 50 ml flask. To this was added sufficient bromine in carbon tetrachloride to give a solution containing 6.13 mmol of bromine. The flask was allowed to stand under room temperature and light conditions. After thirty minutes a 2 ml aliquot was withdrawn and the bromine concentration determined iodometrically. The titer indicated 2.03 mmol of Br_2 remained. The reaction was sampled again after twenty-four and thirty-six hours. The titer (0.20 mmol of bromine) remained the same for these two aliquots. This reaction required 1.02 moles of bromine per mole of cyclopropane.

The remainder of the reaction mixture was evaporated in vacuo in a desiccator over P_2O_5 to yield a light yellow viscous oil.

An infrared spectrum was prepared on this material both neat and in a carbon tetrachloride solution. The fingerprint region (1,400 cm^{-1} to 200 cm^{-1}) was saturated with bands. The aliphatic carbon-hydrogen stretch region, 2800 cm^{-1} to 3000 cm^{-1}, showed two broad bands. A molecular weight determination and a carbon, hydrogen, and bromine analysis also indicated a mixture of products.

The remaining material was transferred to an alembic still and an attempt made to distill under gentle heating at 0.01 torr. No distillate was obtained upon heating to 150°C and the previously pale yellow crude product was altered to brownish-black tar.

Another reaction mixture was prepared using approximately the same concentrations and conditions. A small portion of the reaction mixture was taken up in a syringe and spotted on a 0.25 mm silica gel H thin layer chromatography (t.l.c.) plate (20 X 20 cm). Various other mixtures were also spotted on this plate in the conventional manner as controls. The plate was developed with a benzene: heptane (2:1) solvent mixture to a solvent front distance of about 10 cm. After allowing the plate to dry thoroughly a solution (2%) of formaldehyde in concentrated sulfuric acid was placed on the plate using an eye dropper. The reaction mixture after development showed five bands in all. In order from the solvent front these were (1) a dense, dark brown, (2) a faint yellow streak, (3) another yellow streak, (4) a light pink and (5) a light brown. Pure starting material gave a purple spot nearly at the solvent front. Mixtures of reaction product and starting material gave the same color pattern with the exception that the dense brown spot (from the reaction mixture) was shaded with a purple leading edge (starting material). Spotting with carbon tetrachloride and with bromine in carbon tetrachloride gave no colors. Reaction mixtures from cis-1, 2-diphenylcyclopropane appeared identical to the trans mixtures.

Using the same reaction mixture a 1 mm silica gel H plate (20 X 20 cm) was streaked using a 1 ml syringe. Approximately one fourth of the reaction mixture was placed on the plate in a band about 6-7 mm in width. The plate was developed as above and allowed to dry. Each edge of the plate was treated with the formaldehyde-sulfuric acid solution. Only three distinct bands were readily discernible. A dense dark brown leading band (band I) about 2 cm in width, followed by a yellow band (band II) 3 cm in width and then a light brown band (band III).

The untreated areas were shaved off in three separate bands using the developed edges as a horizontal guide. Each portion was washed three times with ether. The etheral solutions were filtered and then dried over anhydrous K_2CO_3 and evaporated at 35°C in a vacuum oven.

The eluent from band III was less than 10 mg after evaporation. The eluent from band I after evaporation was a nearly colorless, viscous liquid. This was identified as a mixture of d,l and meso-1, 3-dibromo-1, 3-diphenylpropane by its counter synthesis (below) and the following physical properties:

Analysis

	%C	%H	%Br
Calculated ($C_{15}H_{14}Br_2$)	50.88	3.98	45.14
Found	50.83	4.02	45.27

Infrared (Appendix I, Spectrum #17) 2910, 2840, 1260, 695 (broad) and 600 cm^{-1} (a doublet). NMR (Spectrum #16, Appendix II) multiplets centered at 2.90 ppm, 4.80 ppm, and 5.12 ppm and a singlet at 7.31 ppm. Molecular Weight; Calculated 354.0, Found 345.

Synthesis of 1,3 diphenyl-1, 3-propandiol (114)

A solution of 106 g (1.0 moles) of benzaldehyde in 300 ml of glacial acetic acid was placed in a 1 liter round bottom flask and 30 ml of concentrated sulfuric acid added dropwise. Throughout the addition the stirred solution was kept at or below 20°C by means of an ice bath. Next was added, over a forty-five minute period, 104 g (1.0 moles) of freshly distilled styrene. The resulting deep yellow solution was allowed to stand overnight. The flask was placed in an ice bath and 500 ml of H_2O added with stirring. An oil layer separated. Ether was added and the ether layer separated. The ether solution was extracted with H_2O three times and then transferred to a single neck 1 liter round bottom flask. After removal of the solvent on a rotary evaporator, 300 g of a 50% KOH solution was added along with 300 ml of ethyl alcohol. The mixture was refluxed for three hours then stripped of most of the ethyl alcohol on a rotary evaporator. Ether was added and the layers separated. The ethereal solution was extracted four times with H_2O, dried over anhydrous K_2CO_3 and the ether removed under vacuum. A viscous light brown mass was obtained which partially solidified on standing for twenty-four hours. Cold benzene was added and the mixture filtered to obtain a light yellow crystalline material.[1] Recrystallization from benzene gave pure white crystals. M.p. 129-130°; 128-130° (114). Infrared (KBr pellet) 3350 cm^{-1} (broad).

Preparation of 1, 3-dibromo-1, 3-diphenylpropane

To a suspension of 2.7 g (0.012 moles) of 1,3-diphenyl-1, 3-propanediol in 25 ml of heptane, 12 g of PBr_3 was added slowly. The flask was warmed gently and stirred until no solid remained suspended in the solution. The mixture was allowed to stand for one hour during which a heavy syrup appeared in the bottom of the reaction flask. By carefully decanting the heptane layer it was possible to separate the two layers completely. A small portion of the heptane solution was spotted on a 0.1 mm silica gel H plate (20 X 20 cm) along with controls (1, 3-diphenyl-1, 3-propanediol, heptane, reaction product mixture from 1, 2-diphenylcyclopropane (above) and bromine in CCl_4). Development was with benzene/heptane (2:1) to a 10 cm solvent front advance. The plate was dried and covered with the formaldehyde-sulfuric acid developer. A similar chromatogram was obtained for the 1, 2-diphenylcyclopropane reaction mixture as before. The leading intense brown spot also matched the 1, 3-dibromo-1, 3-diphenyl spot both in color and position.

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[1] The filtrate was evaporated and allowed to stand. Additional crystalline material appeared after several days and the entire mass crystallized after two months standing at room temperature.

After evaporation to one-half volume the remaining heptane mixture was streaked on two 1 mm silica gel H plates and developed with the same solvent mixture as above. The edges of the plates were sprayed with the CH_2O-H_2SO_4 mixture to identify the product areas. These areas were shaved off, combined and washed three times with anhydrous ether. Removal of the ether in a vacuum oven at 35° left a nearly colorless, viscous liquid whose infrared spectrum (#18 Appendix I) was identical to that of the 1, 3-dibromo-1, 3-diphenylpropane isolated above. N.M.R. (Appendix II, Spectrum #17); multiplets centered at 2.90ppm, 4.80 ppm, and 5.12 ppm, and a singlet at 7.26 ppm.

Analysis

	%C	%H	%Br
Calculated ($C_{15}H_{14}Br_2$)	50.88	3.98	45.14
Found	50.97	3.78	45.09

In a similar manner the cis isomer of 1, 2-diphenylcyclopropane was reacted with equal molar amounts of bromine in carbon tetrachloride. Chromatograms of the reaction products on 0.1 mm silica gel H were identical to those of the trans isomer. Work up and purification using preparative t.l.c. gave 1, 3-dibromo-1, 3-diphenylpropane as the major reaction product.

Larger scale reactions were carried out and worked up on both the cis and trans isomer in the following manner. In a 50 ml volumetric flask 0.862 g of cis-1, 2-diphenylcyclopropane was placed along with sufficient standard bromine in carbon tetrachloride and carbon tetrachloride to give a solution containing 1.1 moles of bromine per mole of cyclopropane. The flask was stoppered and allowed to stand under room light and at room temperature for twenty-four hours. During this time a total of 6 ml of reaction mixture was removed and the bromine titer determined iodometrically.

One drop of the solution was spotted on a 0.1 mm silica gel H (5 X 20 cm) plate and developed with heptane/benzene (3:1).[1] The remainder of the solution was transferred quantitatively to a 250 ml beaker and evaporated *in vacuo* over P_2O_5 in a desiccator.

A light yellow oil remained which was chromatographed on an alumina column (1.4 X 15 cm). A total of twenty fractions were collected in weighed receivers upon eluting with CCl_4, heptane, ether, ethyl acetate, and acetone. The column packing was extruded and shaken with alcohol and methylene chloride (1:1) for five minutes. This solvent was filtered into a weighed flask.

Using only two drops of liquid from each of the above receivers a 0.1 mm silica gel H (20 X 20cm) plate was spotted. After development with benzene/heptane (2:1), a CH_2O-H_2SO_4 mixture was placed on the plate and the colors and positions of the bands recorded. The receivers were placed in a vacuum over at 35°C and evaporated for twenty-four hours. A total of 1.251 g of material was obtained. On the basis of $C_{15}H_{14}Br_2$, 90.5% of the starting material was recovered after correction for aliquots removed for titration. Of this material 84.2% was recovered as 1, 3-dibromo-1, 3-diphenylpropane.

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[1] This solvent mixture was found to separate authentic samples of pure starting material and the reaction product, 1, 3-dibromo-1, 3-diphenylpropane.

Using a similar procedure, trans-1, 2-diphenylcyclopropane was reacted with bromine in carbon tetrachloride. This reaction mixture was chromatographed on a silica gel (80-200 mesh) (1.4cm X 15cm) column and the eluents treated as above. The following results were obtained: (1) 96.3% of the material was recovered after chromatography, (2) 84% of the recovered material was 1, 3-dibromo-1,3-diphenylpropane.

Several attempts were made to examine the minor reaction products in both of the above reactions. An infrared spectrum (Appendix I, Spectrum #19) was prepared on the material identified as band II (yellow color on t.l.c. with $CH_2O-H_2SO_4$). Molecular weight determinations were made and an N.M.R. spectrum was also prepared on this material. These results will be considered in the discussion.

Reactions of cis-and trans-1-(p-Chlorophenyl)-2-phenylcyclopropane

In a typical reaction 1.24 g (5.4 mmol) of the cis isomer was weighed in a 100 ml volumetric flask. To this was added a standard bromine in carbon tetrachloride solution and carbon tetrachloride to give a solution that contained 1.2 moles of bromine per mole of cyclopropane. The flask was stoppered and allowed to stand at room temperature. A 2 ml aliquot was removed after eight and sixteen hours and the bromine determined iodometrically. The titer did not change between eight and sixteen hours and showed 5.4 mmol of Br_2 had been consumed. A 0.1 mm silica gel H was spotted with this reaction mixture and various controls. The chromotogram was developed using benzene/heptane (2:1) and after drying covered with the $CH_2O-H_2SO_4$ mixture. Three bands were apparent for the reaction mixture. In order from the solvent front they were: Band I- -a dark brown streak; Band II- -a light yellow streak; and Band III- -(just ahead of the spotting area) a light reddish brown spot.

The starting material gave a dark purple spot. The entire chromatogram was very similar to that obtained (above) for the 1,2-diphenylcyclopropane reaction products.

The remainder of the reaction mixture was reduced in volume to about 10 ml and streaked on three 1 mm silica gel H 20 X 20 cm plates. After development and identification of the zones, Band I was shaved from each plate, the powders combined and rinsed with anhydrous ether three times. After filtering, the etheral solution was evaporated in a vacuum oven at 25°C. A very pale yellow viscous liquid was obtained. Attempts at further purification by distillation and gas phase chromatography on this material were unsuccessful. This reaction product was identified by its counter synthesis (below) and the following properties as 1, 3 dibromo-1-(p-chlorophenyl)-3-phenylpropane.

Analysis

	%C	%H
Calculated ($C_{15}H_{13}ClBr_2$)	46.37	3.37
Found	47.91	3.63

Infrared (Appendix 1, Spectrum #20); 2920, 2860, 725, 695 and 645 cm^{-1}.

The *cis* isomer was treated in a similar manner and after workup using preparative t.l.c. a major product was obtained that was identical to that from the *trans* isomer reaction.

Preparation of 1-Phenyl-3-(p-chlorophenyl)-1, 3-propandiol

In a 500 ml round bottom flask fitted with stirrer and dropping funnel was placed 150 ml of glacial acetic acid and 70 g (0.5 moles) of p-chlorobenzaldehyde. After adding 15 ml of concentrated H_2SO_4 (dropwise), 52 g (0.5 moles) of freshly distilled styrene was added dropwise over a thirty minute period. Stirring was continued for one hour after which the pale yellow solution was allowed to stand at room temperature for 72 hours. Ether (200 ml) was added and the mixture stirred briefly then allowed to settle. The ether layer was removed, extracted twice with H_2O and placed in a 500 ml round bottom flask. After removal of the ether on a rotary evaporator, 75 g (1.3 moles) of solid KOH, 100 ml H_2O and 150 ml of 95% alcohol were added. The mixture was refluxed for three hours and then the volume reduced by one-half under reduced pressure. Ether was added to the remaining mixture and the solution stirred for five minutes. The ether layer was separated and extracted with H_2O until neutral to litmus. After removing the ether on a rotary evaporator a light yellow viscous mass remained. Refrigeration for one week failed to yield any crystalline material.[1] This viscous material was used without further purification in the preparation below.

Preparation of 1, 3-Dibromo-1-(p-chlorophenyl)-3-phenylpropane

To a solution of 1 g of the above material in 30 ml of heptane was added excess PBr_3. The mixture was stirred and allowed to stand overnight in a hood. Ether was added, the mixtures stirred and the organic layer removed. After evaporation to less than 20 ml, the ethereal solution was filtered through an alumina column (1.5 X 8 cm) previously wet with ether. The solvent was evaporated leaving a colorless viscous material. The infrared spectrum (Spectrum #21, Appendix I) was identical in all respects to the reaction product of both isomers of 1-(p-chlorophenyl)-2-phenylcyclopropane with bromine in CCl_4 (above).

[1] All attempts to aid crystallization of this material failed. An infrared spectrum (neat-KBr discs) showed a broad OH band and the absence of any carbonyl absorption indicating that the acetate had been hydrolyzed completely and only the diol was present.

Analysis[1]

	%C	%H	%Br
Calculated ($C_{15}H_{13}ClBr_2$)	46.37	3.37	41.13
Found	51.53	3.82	35.73

A large scale reaction on cis-1-(p-chlorophenyl)-2-phenylcyclopropane was carried out. For this reaction 1.244 g of starting material was reacted with a slight excess of bromine in carbon tetrachloride. Upon completion of the reaction, the volume was reduced *in vacuo* in a desiccator over P_2O_5 and the products chromatographed on an alumina (80-200 mesh) column (1.4 X 15 cm). A total of sixteen fractions were collected in weighed receivers. After spotting a 0.1 mm silica gel H plate with each fraction, the solvents were evaporated in a vacuum oven at 35° for 24 hours. Identification of the products using infrared and the t.l.c. information indicated 89% of starting material had reacted to give 1, 3-dibromo-1-(p-chlorophenyl)-3-phenylpropane. Infrared spectra obtained on two other minor components were very similar to that obtained for the major product. One additional band at 1690 cm^{-1} was noted.

Reactions of cis-and trans-1-(p-Fluorophenyl)-2-phenylcyclopropane

Qualitative reactions of both isomers were carried out under laboratory light and the reaction products compared using thin layer chromatography and infrared spectroscopy. The isomers gave identical t.l.c. patterns which were similar to those obtained for 1, 2-diphenylcyclopropane. The infrared spectra (in CCl_4) on the reaction solutions were also identical.

Two larger scale quantitative reactions were carried out on trans-

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[1] Analysis was performed approximately 72 hours from the time of preparation. The sample had changed from colorless to a pale yellow material during this time.

1-(p-fluorophenyl)-2-phenylcyclopropane. For the first reaction 0.512 g was reacted with excess Br_2 in CCl_4. Upon completion of the reaction (as indicated by t.l.c.) the reaction mixture was chromatographed on an alumina (dried at 110° for two hours) column (1.4 cm X 15 cm). The mixture was eluted with benzene/heptane (2:1) and collected in nine fractions. More than 77% of the reaction product was identified as 1, 3-dibromo-1-(p-fluorophenyl)-3-phenylpropane by the following properties. IR, (Spectrum #22, Appendix I) 2950, 2910, 2850, 590, and 570 cm^{-1}. N.M.R., (Spectrum #19, Appendix II); multiplets centered at 2.90 ppm, 4.96 ppm and 7.20 ppm.

Analysis

	%C	%H	%Br
Calculated ($C_{15}H_{13}Br_2F$)	48.51	3.52	42.95
Found	48.10	3.44	43.19

Another large scale reaction of the trans isomer was carried out using 0.650 g of the cyclopropane. This reaction mixture was chromatographed on a silica gel (80/200 mesh) column (1.4 X 15 cm). The products were eluted in four fractions using benzene/heptane (2:1). Using t.l.c. to observe the purity of the fractions, 95% of the theoretical amount of 1, 3 dibromo-1-(p-fluorophenyl)-3-phenylpropane was recovered. The infrared spectrum was identical to that obtained for this same compound from the previous reaction.

Reaction of trans-1-(p-Methoxyphenyl)-2-phenylcyclopropane

Qualitative reactions of both cis-and trans-1-(p-methoxyphenyl)-2-phenylcyclopropane were carried out under laboratory light conditions and the reaction products compared using t.l.c. and infrared spectroscopy. No difference between the reaction products from the two isomers could be observed. The t.l.c. patterns were similar to those obtained for other reaction product mixtures above.

A larger scale reaction was carried out using 1.995 g of the trans isomer with a 1.1 times excess of bromine in 100 ml of carbon tetrachloride. The reaction was carried in a glass stoppered pyrex vessel at a distance of four feet from a GE-AH-4 mercury vapor lamp. A Corning filter (#5031) was used to eliminate radiation below 320 mμ. Upon completion of the reaction (t.l.c.) the volume of the solution was reduced to ca. 10 ml by evaporation in vacuo.[1] The solution was placed on an alumina column (1.4 X 15 cm)[2] and eluted with benzene: heptane (2:1), chloroform, ether and acetone. A total of nine fractions were taken which were spotted on a 0.1 mm silica gel H plate (20 X 20 cm) to observe the purity of the fractions. The fractions were combined into three flasks and evaporated in a vacuum oven at 35°C. Two fractions[3] (88%) had identical infrared spectra (Spectrum #23, Appendix I) 1678 and 590-570 (doublet) cm^{-1} in addition to bands found in the previous 1, 3-dibromo reaction products. Molecular Weight: found 379, Calculated ($C_{16}H_{16}Br_2O$) 384. The N.M.R. spectrum indicated a mixture of compounds present.

Attempted Preparation of 1, 3-Dibromo-1-(p-methoxyphenyl)-3-phenylpropane (114)

In a 1 liter, three necked round bottom flask fitted with stirrer and dropping funnel were placed 100 ml of glacial acetic acid, 10 ml of concentrated H_2SO_4 (dropwise) and 45 g (0.33 moles) of anisaldehyde. To this rapidly stirred, deep red solution 35 g (0.33 moles) of styrene was added over a 25 minute period while the temperature was maintained at 20 ± 1°C. The now amber colored solution was allowed to stand at room temperature overnight. Water, 170 ml, was added followed by 200 ml of ether. The ethereal layer was decanted, washed three times with H_2O and evaporated on a rotary evaporator. To the viscous amber mass that remained was added 50 g KOH, 120 ml H_2O and 100 ml ethyl alcohol. This mixture was refluxed for 3.5 hours, cooled, extracted with ether and the ethereal layer separated. After extracting the ethereal solution with H_2O three times and drying over anhydrous K_2CO_3 the ether was removed under vacuum. A light yellow syrup remained which failed to crystallize.[1]

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[1] When the stopper was removed some HBr was observed visibly.

[2] A dark red band formed at top of column which was removed when the ether-acetonemixture eluted it.

[3] This material was pale yellow initially and changed to dark brown on exposure to air. The material used for the infrared spectrum became dark brown during the course of preparation of the spectrum. The infrared spectrum in CCl_4 was the same as the spectrum obtained neat on KBr discs.

To 5 g of this syrupy diol in 50 ml of ether was added slowly 15 g of PBr_3. After standing overnight two layers appeared. The upper layer was decanted and the ether removed in vacuum leaving light yellow material[2] whose infrared spectrum (Spectrum #24, Appendix I) was nearly identical to that for the reaction product from the corresponding cyclopropane with Br_2 in carbon tetrachloride. The N.M.R. spectrum (#20, Appendix II) indicated a mixture of products.

Reactions of cis- and trans-1-(m-chlorophenyl)-2-phenylcyclopropane

Qualitative reactions of both isomers were carried out with bromine in carbon tetrachloride under laboratory light conditions. The products from the reactions of the isomers gave identical t.l.c. patterns which were similar to those obtained above for the other cyclopropanes. A larger scale reaction was carried out in the following manner. The trans isomer 1.32 g (5.79 mmol) was weighed into a 50ml volumetric flask. The flask was filled with a 0.2 molar Br_2 in CCl_4 solution (2:1 excess bromine to cyclopropane). The flask was photolysed at a distance of three feet from a GE-AH-4 mercury vapor lamp fitted with a Corning filter (#5031). After all of the cyclopropane had reacted (three hours) the solution was evaporated and chromatographed on a silica gel column (1.4 X 15 cm), using benzene:heptane (2:1). The fractions were collected in weighed receivers and evaporated in a vacuum oven at 35°C. The major fraction was similar to the reaction products from the previous reactions and was obtained as 81% of the material collected. It had the following properties. Molecular weight: found 390; calculated (for $C_{15}H_{13}Br_2Cl$) 388. N.M.R. (Spectrum #21, Appendix II); multiplets centered at 2.90,4.90 ppm, and 7.25 ppm. IR (Spectrum #25, Appendix I) 2970-50 (doublet), 2900, 2850, 593 and 550 cm^{-1}.

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[1] The infrared spectrum of this material showed strong OH absorption and the absence of any carbonyl absorption. With the exception of the methoxy group absorptions the spectrum was very similar to those obtained for the previously prepared diols.

[2] This material also decomposed to a dark brown tar when exposed to air.

Analysis

	%C	%H	%Br
Calculated ($C_{15}H_{13}Br_2Cl$)	46.37	3.37	41.14
Found	46.01	3.38	41.17

EXPERIMENTAL PART IV

This section pertains to the experiments performed to examine the kinetics of the reactions of 1, 2 diarylcyclopropanes with bromine in carbon tetrachloride. Two types of experiments were performed to this end. The first was the photolysis of reaction mixtures in a flow system (described below) using only one compound at a time. The second treated the simultaneous photolysis in silica cells (1 cm) of the different compounds to obtain relative kinetic relationships.

A flow system (figure 1) was constructed using a Beckman solution metering pump with Teflon fittings, Teflon tubing (0.15" i.d.), a quartz photolysis cell (3 feet of 8mm quartz folded into a square radiator 7" X 7") and a Beckman ultraviolet flow cell in a Beckman DK-1A ultraviolet spectrophotometer.

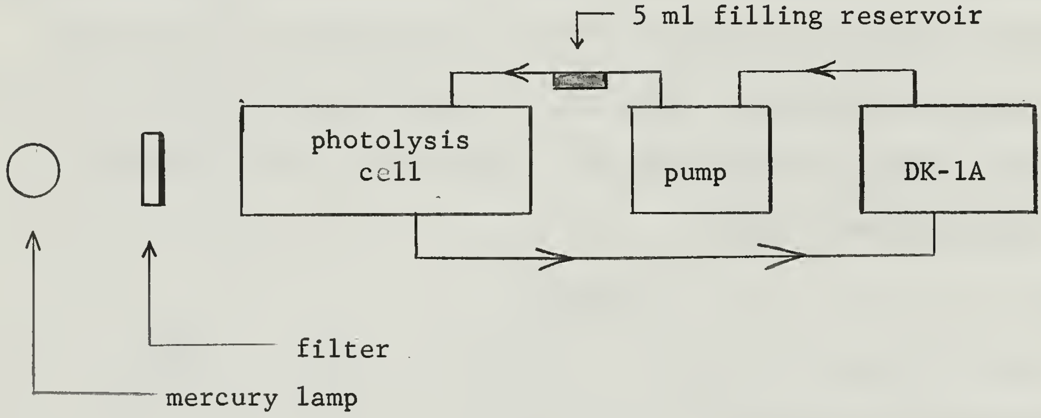

Figure 1

Photolysis was carried out using a GE-AH-4 mercury lamp with a Corning filter #5031. Black felt was used to protect the tubing and pump from irradiation so that only the photolysis cell was exposed to any radiation.[1] The total volume of the system was 35 ml.

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[1] Preparation of the reaction mixtures, mixing and filling was carried out in total darkness with the exception of light from a small flash light which was used as necessary.

An initial check on the system was done using 0.1 molar bromine in carbon tetrachloride. This solution was cycled through the system under photolysis conditions for one hour. A continuous recording of the absorbance was made at 580 mμ. No change of absorbance was observed during this time. Additional checks were made by circulating reaction mixtures through the system for several minutes prior to photolysis for each run made. No change in absorbance was noted during any of these checks due to either evaporation of the bromine or dark reaction with the cyclopropane. The data for the kinetic runs that followed are listed in Appendix III.

Kinetic Run #9[1]

For this run the flow system described above was altered to include a cell[2] of 1cm path length placed in a Perkin-Elmer Model 621 Infrared Spectrophotometer. Continuous scans (1 minute) from 3200-2700 cm^{-1} were recorded during this run.

The reaction mixture was prepared by mixing equal volumes of 0.2 molar bromine in CCl_4 with 0.2 molar trans-1, 2-diphenylcyclopropane.[3] The absorbance was measured at 600 mμ for the initial portion of the reaction followed by measurement at 550 mμ.

[1] A series of preliminary kinetic runs were made under varying conditions in an attempt to determine the optimum conditions and systems to use in these measurements.

[2] The cell was made from NaCl discs with an insert of 1" diameter Teflon tubing fitted with an inlet (bottom) and outlet (top). Teflon fittings were machined for the inlet and outlet to accommodate the Teflon flexible tubing of the flow system.

[3] The carbon tetrachloride used for runs 9 and 10 was spectrograde and showed very little carbon-hydrogen absorption when measured in a 5 cm path length cell from 2700-3200 cm^{-1}.

Kinetic Run #10

The flow system as described for kinetic run #9 was used with the exception that the infrared cell was reduced to 5mm path length. The reaction mixture was prepared by weighing 1.029g (0.053 moles) of trans-1, 2-diphenylcyclopropane into a 100ml volumetric flask, adding 25 ml of 0.213 molar Br_2 in CCl_4 and diluting to 100 ml with CCl_4. After mixing, the reaction mixture was placed in the flow system and circulation begun. The mixture was circulated for 20 minutes before photolysis was begun. (Although the average absorbance remained constant during this time the absorbance versus time plot was a sinusoidal wave symetric about A = 0.90. The amplitude of the waves diminished from $\Delta A = 0.02$ to less than $\Delta A = 0.005$ during this time period. This same wave feature was observed (usually to a lesser extent) in all of the kinetic runs using this flow system and was felt to be caused by the restricted mixing available within the flow system and the discontinuous nature of the pumping. The period of the waves corresponded to the time for one complete circulation through the system.) The change in absorbance with time was recorded at 565 mμ and at 500 mμ.

Kinetic Run #11

The flow system used for this run was as described in Figure 1.

In a 50 ml flask 0.585g (2.56 mmols) of trans-1-(p-chlorophenyl)-2-phenylcyclopropane was weighed. To this was added 12.00 ml of 0.213 M bromine in CCl_4 and the flask filled to the mark with CCl_4. The solution was mixed thoroughly and placed in the flow system and allowed to circulate for 9 minutes before photolysis was begun. The change in absorbance with time was recorded at 570 mμ and 529 mμ .

Kinetic Run #12

It was attempted in this run to make conditions identical with run

#11. To this end the flow system was disassembled at the completion of run #11, cleaned thoroughly and dried in an oven at 50°C. The flow system was reassembled and positioned exactly as in run #11. After weighing 0.442 g of trans-1, 2-diphenycyclopropane into a 50 ml flask, 10.7 ml of 0.213 M Br_2 in CCl_4 was added. The flask was filled to the mark giving a mixture 0.046 molar in cyclopropane and 0.0455 molar in bromine. The reaction mixture was placed in the flow system and allowed to circulate for 11 minutes prior to photolysis. The change in absorbance with time was recorded at 570 and 530 mμ.

Kinetic Run #13

For this run the filling reservoir and portions of the tubing were placed in a constant temperature bath at 25°C. In a 50 ml flask 0.6087 g of trans 1-(p-methoxyphenyl)-2-phenycyclopropane was placed with 12.60 ml of 0.0543 molar bromine in carbon tetrachloride. The flask was filled to the mark, mixed thoroughly and placed in the flow system. After allowing circulation for 7 minutes in the dark, photolysis was started and the change in transmission with time recorded at 570 mμ. Several bubbles became entrapped in the flow system while filling. The presence of these in the flow cell in the spectrophotometer caused considerable "noise" to be present in the recorded output.

Kinetic Run #14

The flow system as depicted in Figure 1 was used for this run with one alteration. The filling reservoir was altered to give a small stand pipe in which bubbles flowing through the system would be removed after one cycle. For this run a solution was prepared that was 0.0493 molar in trans-1-(p-methoxyphenyl)-2-phenylcyclopropane and 0.054 molar in bromine. The solution was circulated for 7 minutes prior to photolysis. The change in transmission with time was recorded at 570 mμ.

Kinetic Run #18.

The flow system in Figure 1 was used for this run. The system was filled with a solution that was 0.0513 molar in both bromine and cis-1-(p-chlorophenyl)-2-phenylcyclopropane. The solution was circulated for ten minutes before photolysis was begun. Transmission versus time was recorded at 570 mμ.

Kinetic Run #19.

Conditions were identical to run #18. The flow system was filled with a solution that was 0.0492 molar in bromine and trans-1-(p-chlorophenyl)-2-phenylcyclopropane. After circulation for 10 minutes photolysis was begun and the change in transmission with time recorded at 570 mμ.

Kinetic Run #20.

Conditions were identical to run #18. A solution 0.0455 molar in bromine and cis-1, 2-diphenylcyclopropane was prepared and placed in the flow system. Photolysis was begun after the solution had circulated in the dark for 12 minutes. The change in transmission with time was recorded at 570 mμ.

Kinetic Run #21.

For this run a solution 0.0468 molar in bromine and cis-1, 2-diphenycyclopropane was placed in the flow system and allowed to circulate in the dark. Photolysis was begun after 10 minutes and the change in transmission with time was recorded at 570 mμ. All other conditions were identical to run #20.

Kinetic Run #22.

Conditions for this run were identical to run #21. A solution was prepared that was 0.0521 molar in bromine and in trans-1, 2-diphenylcyclopropane. The flow system was filled and photolysis begun after 10 minutes of circulation in the dark. The change in transmission with time was recorded at 570 mμ.

In Table II are listed a summary of kinetic runs 9-22. The significance and interpretation will be considered in the discussion.

Kinetic Runs 28-47 were conducted in the following manner to obtain relative rates of reaction for the series of cis and trans cyclopropanes prepared. Samples of cyclopropanes were weighed into 25 ml volumetric flasks and diluted with bromine in carbon tetrachloride to give solutions that were equimolar in reactants. (Except in several runs where a large excess of either cyclopropane or bromine is indicated.) Within a particular run it was attempted to keep the concentrations of the cyclopropanes as equal as possible. The solutions were diluted and mixed in nearly total darkness after which a portion of each was used to fill a 1 cm silica cell. After measuring the initial absorbance at 420 mμ the cells were placed at one of the photolysis positions indicated in Figure 1a.

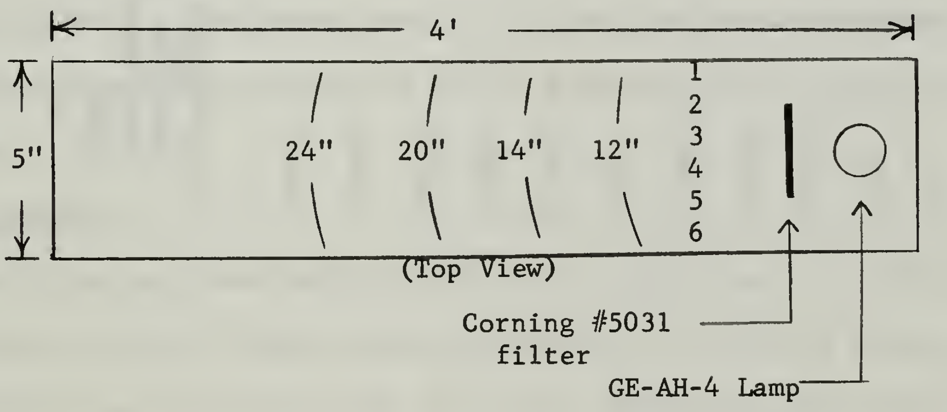

Figure 1a

The cells were arranged in an arc whose radius was equal to the distance from the lamp. Measurements of the change in absorbance were made at

Summary of Kinetic Runs 9-22

Run #	Br_2 (m/l)	Compound		(m/l)	Plot $1/\sqrt{A}$ vs. time[a]
9	0.10	trans	p-H	0.10	linear
10	0.053	trans	p-H	0.053	linear
11	0.0512	trans	p-Cl	0.0511	linear
12	0.0455	trans	p-H	0.0460	linear
13	0.0453	trans	p-CH_3O	0.0543	linear
14	0.054	trans	p-CH_3O	0.0493	linear
18	0.0513	cis	p-Cl	0.0513	linear (0.0188)
19	0.0492	trans	p-Cl	0.0492	linear (0.0113)
20	0.0455	cis	p-H	0.0455	linear (0.0112)
21	0.0468	cis	p-H	0.0468	linear (0.0169)
22	0.0521	trans	p-H	0.0521	linear (0.0157)

(a) Conditions for runs 18-22 were kept as identical as possible. The number indicated for these runs is the slope (min^{-1}) from the graph of a plot of $1/\sqrt{A}$ versus time.

TABLE II

various time intervals by covering the lamp and placing the cells in the spectrophotometer.[1] To eliminate position (of the cell during photolysis) bias the cells were rotated through the six positions labeled in figure 1a after each time interval measurement. To eliminate cell bias, each cell was used for all of the compounds during the different runs (i.e. trans-1, 2-diphenylcyclopropane was photolyzed in all six of the silica cells used in these runs). The data for the kinetic runs that follow are listed in Appendix III. In each case a plot of $1/\sqrt{A}$ versus time was made and the slope of the line recorded. In the runs that follow only the isomer and the substituent are given when referring to the parent compound. For example trans para H is listed for trans-1, 2-diphenylcyclopropane and cis-1-(p-chlorophenyl)-2-phenylcyclopropane is given as cis para Cl.

Kinetic Run #28.

For this run the following solutions were prepared: 0.0385 molar in trans para H, 0.0423 molar in trans para Cl and 0.0360 molar in trans para CH_3O. The initial concentration of bromine was measured at 420 mμ (ϵ_{420} 208.1). An approximate 10:1 excess cyclopropane;bromine was used here. Photolysis was carried out at a distance of 14 inches from the lamp.

Kinetic Run #29.

The following concentrations were used in this run: 2.89 mmolar trans para Cl and 2.91 mmolar trans para CH_3O-. The initial bromine concentration was determined from the initial absorbance measurement prior to photolysis. Photolysis was carried out at a distance of 14 inches from the lamp.

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[1] For these runs either a Beckman Model DU or Beckman Model DB was used and is indicated with each run in Appendix III.

Kinetic Run #30.

Solutions for this run were prepared to give approximately equal molar amounts of bromine and the cyclopropane. The solutions were 2.62 mmolar cis para H, 2.56 mmolar cis para Cl and 2.76 mmolar cis para CH_3O. Photolysis was carried out at a distance of 14 inches from the lamp and absorbance measurements made at 420 mμ. At the completion of the kinetic run a 0.25 mm silica gel H plate (20 X 20 cm) was spotted with each of the reaction mixtures without photolysis, each reaction mixture with photolysis and each of the pure cyclopropanes. The plate was developed to a solvent front distance of 12 cm in benzene/heptane, 2:1. After drying thoroughly the plate was covered with a two percent solution of formaldehyde in concentrated sulfuric acid. A photograph was taken immediately and appears in Appendix IV.

Kinetic Run #32.

This kinetic run was carried out using a large excess of bromine. Trans para H (0.0717 g) was weighed into a 25 ml volumetric flask to which was added a solution of bromine in carbon tetrachloride to give a twentyfold molar excess of bromine to the cyclopropane. The reaction mixture was placed in a silica cell at a distance of 14 inches from the lamp. Aliquots (0.20 ml) were removed initially and periodically during photolysis. These aliquots were quenched by adding them to 0.50 ml of a 60% (by volume) cyclohexene, chloroform solution. Analysis was carried out quantitavely for the amount of cyclopropane remaining via g.p.c. (oven temperature of 210°C was used here along with the equipment and conditions described in part I of the experimental section).

Kinetic Run #34.

The following solutions were prepared: 3.28 mmolar trans para H, 3.40 mmolar trans para Cl, 3.34 mmolar trans para F, 3.28 mmolar trans meta Cl and 3.25 mmolar *trans* para CH_3O. Bromine in CCl_4 was used to give approximately equal molar concentrations. Photolysis was carried out at a distance of 20 inches from the lamp and absorbance measurements made at 420 mμ.

Kinetic Run #35.

This was a duplication of run #34 using solutions of the following concentrations: 4.24 mmolar *trans* meta Cl, 4.31 mmolar *trans* para F, 4.06 mmolar *trans* para H, 4.17 mmolar *trans* para Cl and 4.28 mmolar *trans* para CH_3O.

Kinetic Run #36.

This run was a duplication of run #34 using the following solutions: 3.28 mmolar *trans* meta Cl, 3.11 mmolar *trans* para H, 3.20 mmolar *trans* para Cl, 3.04 mmolar *trans* para CH_3O, and 3.30 mmolar *trans* para F.

Kinetic Run #37.

This run was a duplication of run #34 using the following solutions: 2.93 mmolar *trans* para CH_3O, 3.02 mmolar *trans* para F, 3.19 mmolar *trans* meta Cl, 3.12 mmolar *trans* para H and 3.19 mmolar *trans* para Cl.

In the Table III below are summarized the data of Kinetic Runs #28 to #37 (excluding #30 on *cis* isomers). The slopes pertain to the initial slope from a plot of $1/A$ versus time for runs in which the concentration of bromine and cyclopropane were approximately equal. No corrections are given here for any deviations from equal molar conditions. Only the absolute slope is given for each compound in each run.

Kinetic Run #38.

The following solutions were prepared for this run: 3.36 mmolar *cis* para H, 3.23 mmolar *cis* para Cl, 3.17 mmolar *cis* meta Cl, and 3.52 mmolar *cis* para CH_3O. Photolysis was carried out at 20 inches from the lamp and absorbance measurements made at 420 mμ.

Summary of Kinetic Runs on *trans* Isomers

Absolute Slopes (X 10^4 Sec.)

Run #	para H	para Cl	para F	para CH_3O	meta Cl
28*	7.15	6.20	- -	11.7	- -
29	4.45	4.04	- -	5.40	- -
32**	- -	- - -	- -	- -	- -
34	3.08	2.74	2.80	3.67	1.98
35	1.83	1.47	1.76	2.54	1.12
36	1.50	1.34	1.50	2.07	1.14
37	1.85	1.63	1.76	2.98	1.27

*This run used 10:1 excess cyclopropane and the slopes (X 10^3) refer to a plot of $\sqrt{A}$ vs. time.

**This run used 20:1 excess bromine for para H only.

TABLE III

Kinetic Run #39.

This run was a duplication of run #38 using the following solutions: 3.05 mmolar cis para H, 3.26 mmolar cis para Cl, 3.42 mmolar cis meta Cl, and 2.68 mmolar cis para CH_3O.

Kinetic Run #40.

A duplication of run #38 using the following solutions: 3.86 mmolar cis meta Cl, 3.93 mmolar cis para H, 3.82 mmolar cis CH_3O, and 3.19 mmolar cis para Cl.

Kinetic Run #41.

The following solutions were prepared for this run: 3.38 mmolar cis para H, 3.41 mmolar cis para CH_3O, 3.37 mmolar cis meta Cl, and 3.37 mmolar cis para F. Photolysis was carried out at a distance of 24 inches from the lamp and absorbance measurements made at 420 mμ.

Kinetic Run #43.

A tenfold excess of the cyclopropane to bromine was used for this run. Solutions were 0.0354 molar cis para Cl, 0.0346 molar cis meta Cl, 0.0367 molar cis para H, and 0.0294 cis para CH_3O. Photolysis was carried out at 20 inches from the lamp and absorbance measurements made at 420 mμ.

Kinetic Run #44.

This run was a duplication of run #38 using the following solutions: 3.25 mmolar cis para F, 3.42 mmolar cis para CH_3O, 3.54 mmolar cis para Cl, 3.09 cis meta Cl and 3.22 cis para H. In addition a solution of trans para H (3.27 mmolar) was run along with the above cis compounds.

Kinetic Run #45.

The following solutions were prepared for this run: 3.73 mmolar cis para CH_3O, 3.59 mmolar trans para H, 3.32 mmolar cis meta Cl, 3.22

mmolar cis para H, 3.15 mmolar cis para F and 3.33 mmolar cis para Cl. Photolysis was carried out at a distance of 12 inches from the lamp and absorbance measurements made at 420 mμ.

Kinetic Run #45a.

The excess unphotolyzed solutions from run #45 were used for this run at the completion of run #45. Different cells were used for each solution in this run than were used for run #45.

Kinetic Run #46.

A ten fold excess of the cyclopropanes was used for this run. Solutions were 0.0488 molar cis meta Cl, 0.0464 molar cis para H, 0.0467 cis para F, 0.0415 molar cis para CH_3O and 0.0562 molar cis para Cl. Photolysis was carried out at 20 inches and absorbance measurements made at 420 mμ.

A summary of these runs is given in Table IV below.

Kinetic Run #47a.

This run was carried out to obtain relative rates of reaction between the cis and trans isomers of para H. Solutions were prepared that were 3.21 mmolar in both cis and trans para H. Three photolysis cells were filled with each solution and the cells placed in the 12 inch arc (Figure 2) so that adjacent positions were occupied by different isomers. Absorbance measurements were made at 420 mμ initially and after approximately one half of the bromine present had been consumed.

Kinetic Run #47b.

This run was a duplication of run #47a using solutions cis and trans meta Cl (2.60 mmolar for each) with approximately equal molar amounts of Br_2.

Kinetic Run #47c

This run was a duplication of run #47a using solutions of cis and

Summary of Kinetic Runs on Cis Isomers

Absolute Slopes (X 10^4 X Sec.)

Run#	para H	para Cl	para F	meta Cl	para CH_3O
30	2.54	2.33	- -	- -	2.93
38	2.38	1.97	- -	1.73	3.05
39	2.70	2.30	- -	2.00	3.48
40	2.95	2.65	- -	2.40	3.97
41	0.92	0.78	- -	0.68	1.80
43*	0.68	0.55	- -	0.54	1.78
44	2.60	2.30	2.35	2.10	3.30
45	2.42	1.95	2.10	1.48	3.24
45a	2.33	1.74	2.23	1.55	3.12
46*	1.21	1.00	1.12	1.04	1.82

*A tenfold excess cyclopropane was used for this run. The slope refers to the $\sqrt{A}$ versus time.

TABLE IV

trans para CH_3O (2.54 mmolar for each) with approximately equal molar amounts of Br_2.

Table V below summarizes the results for comparison of rate between isomers and includes data from three other runs for which comparisons are available. The data is given as the ratio of the amount of each isomer reacted within the same time period and is the average of that obtained from the three pairs of measurements made.

Determination of Quantum Yield for Photochemical Addition of Bromine to *trans*-1, 2-Diphenylcyclopropane

A series of runs were made using carbon tetrachloride solutions of *trans*-1, 2-diphenylcyclopropane and bromine. The solutions contained sufficient bromine such that under the photolysis conditions total absorption of the incident radiation occurred. Photolysis was carried out using a Hanovia 200 watt mercury lamp. The lamp was placed at a distance of 12 cm from a 1 X 2 cm slit. A second slit (1 X 2 cm) was placed 3 cm behind the first slit to provide an approximately parallel beam for photolysis. A Corning filter (#5113) was placed immediately behind the second slit. The characteristics of this filter were measured on a Beckman DK1A spectrophotometer. A symmetric envelop of high transmission was obtained for 50 mμ on both sides of 390 mμ . Transmission was less than 15% at 320 mμ and less than 1% at 310 mμ and below. On the longer wave length side transmission was less than 15% at 460 mμ and less than 10% at 480 mμ and above. Due to the characteristics of the lamp and this filter then all of the radiation incident on the photolysis solutions was between 450 and 350 mμ. Photolyses were carried out in a glass stoppered, pyrex vessel immediately behind the filter.

A uranyl nitrate-oxalic acid solution was used as an actinometer (21[illegible])before and after the photolytic reactions involving the cyclopro-

Summary of Kinetic Runs on *Cis* and *Trans* Isomers

Run #	Compound	Ratio (*trans*:*cis*)
44	para H	1.19*
45	para H	1.07*
45a	para H	1.08*
47a	para H	1.14**
47b	meta Cl	1.02**
47c	para CH_3O	1.07**

*This value obtained from the ratio of the slopes from a $1/\sqrt{A}$ versus time plot for each reaction mixture.

**This ratio obtained from ratio of the change in absorbance after photolysis for equal times for each solution.

TABLE V

pane. A solution (75 ml) was prepared that was 0.005 molar in uranyl nitrate and 0.0025 molar in oxalic acid. A 25 ml aliquot was removed and titrated with 0.004 molar standardized $KMnO_4$. The remainder of the solution was placed in the photolysis cell and irradiated for nine hours. At the end of this time another 25 ml aliquot was removed and titrated. From the change in titer it was determined that under these conditions 0.0132 μmoles of oxalic acid were decomposed per ml-minute. Using a quantum yield of 0.55 (21a)this corresponds to 0.0240 μmoles per ml-minute. In a similar determination where photolysis covered a three hour period a value of 0.0229 μmoles per minute.

Three runs were made on bromine and trans-1, 2-diphenylcyclopropane carbon tetrachloride solutions using varying concentrations. For run #1 a solution was prepared that was 0.010 molar in bromine and 0.0046 molar in cyclopropane. The solution was photolyzed in a manner identical to that of the actinometer for 33 minutes. The concentration of bromine was determined colorimetrically before and after photolysis and the amount reacted calculated to be 0.043 μmoles per ml-minute. This corresponds to a quantum yield of 1.8. A second run was made using a solution that was 0.0076 molar in the cyclopropane and 0.0181 molar in bromine. Photolysis was carried out for 35 minutes and a total of 0.049 μmoles per ml-minute were reacted. This corresponds to a quantum yield of 2.1.

A third run was made using a solution 0.0191 molar in the cyclopropane. For this run 0.171 μmoles per ml-minute was reacted which corresponds to a quantum yield of 7.3.

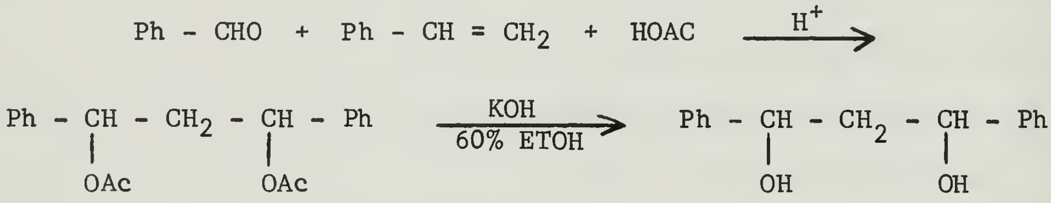
An attempt to use malachite green leucocyanide was also used under these same conditions. The dye was prepared and used as outlined by

Calvert and Ricken (11a). Under these conditions no photolysis was observed for exposure times of up to one hour. Since the dye requires radiation of 310 mμ and below for photolysis, the filter and slit system was demonstrated to provide the desired radiation.

DISCUSSION

Discussion of Preparation, Purification, and Identification of 1, 2-Diarylcyclopropanes

To carry out the investigation of the ring cleavage of 1, 2-diarylcyclopropanes a series of these compounds were prepared. As indicated in the Historical Section many general techniques are available for the synthesis of cyclopropanes. Not all of these are applicable to the synthesis of 1, 2-diarylcyclopropanes. Most of the elimination reactions cited are applicable to this type of synthesis but overall yields are usually low. For example to utilize the Gustavson reaction for the preparation of 1, 2-diphenylcyclopropane a multistep synthesis is utilized as follows: Benzaldehyde is condensed with styrene in acetic acid in the presence of sulfuric acid to give the 1, 3-diacetate XXI. Refluxing of XXI in alcoholic KOH yields the 1, 3 diol XXII (114).

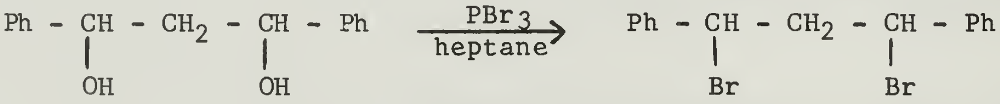


$$\mathrm{Ph-CHO} + \mathrm{Ph-CH=CH_2} + \mathrm{HOAC} \xrightarrow{H^+}$$

$$\mathrm{Ph-\underset{OAc}{CH}-CH_2-\underset{OAc}{CH}-Ph} \xrightarrow[\text{60\% ETOH}]{\text{KOH}} \mathrm{Ph-\underset{OH}{CH}-CH_2-\underset{OH}{CH}-Ph}$$

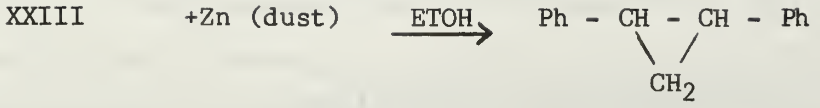
XXI XXII

Reaction of XXII with phosphorus tribromide in heptane at low temperatures gives the desired 1, 3-dibromo compound XXIII (3,48). The action of zinc dust on XXIII affords the desired cyclopropane XXIV. Overall yields for this reaction are usually less than 10%.



$$\mathrm{Ph-\underset{OH}{CH}-CH_2-\underset{OH}{CH}-Ph} \xrightarrow[\text{heptane}]{\mathrm{PBr_3}} \mathrm{Ph-\underset{Br}{CH}-CH_2-\underset{Br}{CH}-Ph}$$

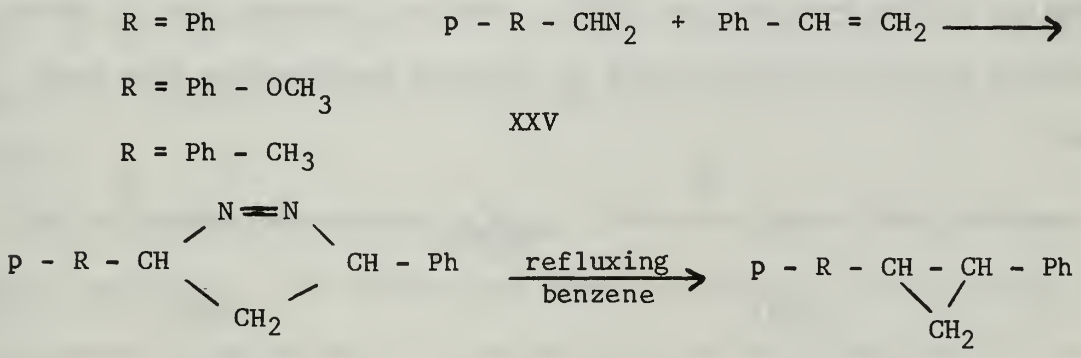
XII XXIII



$$\text{XXIII} + \text{Zn (dust)} \xrightarrow{\text{ETOH}} \text{Ph - CH - CH - Ph}\ (\text{CH}_2)$$

XXIV

In this work only two types of syntheses were utilized for the preparation of the desired cyclopropanes. The first, the thermal decomposition of 1-pyrazolines, was utilized only for the preparation of trans isomers of 1, 2-diphenyl-, 1-(p-methylphenyl)-2-phenyl- and 1-(p-methoxyphenyl)-2-phenyl-cyclopropanes. The yield in each case was poor in spite of the fact that the 1-pyrazoline (XXVI) decomposes quantitatively to the desired cyclopropane (74). In no case was any of the cis isomer obtained. The instability of the 1-pyrazolines as well as the poor yields from the addition of the substituted phenyldiazomethanes (XXV) to styrene resulted in overall yields of less than 20%.



XXVI

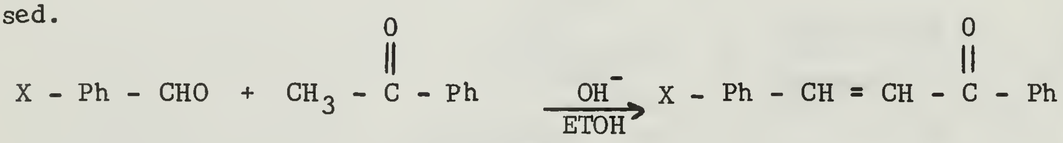
The preparation of 1-(p-chlorophenyl)-2-phenylcyclopropane was attempted using this route but none of the desired cyclopropane was obtained. Good yields, however, have been reported for the synthesis of the symmetrically substituted 1, 2-bis-(p-chlorophenyl)-cyclopropane (74). The general trend observed here is that the symmetrically substituted 1-pyrazolines are more easily formed and more stable than the similar, unsymmetrically substituted pyrazolines. Table VI summarizes the yields obtained for the trans cyclopropanes from the 1-pyrazolines.

Cyclopropanes from 1-Pyrazolines

Compound	Isomer	Percent yield (overall)
1, 2-diphenyl-	trans	18
1-(p-methylphenyl)- 2-phenyl-	trans	15
1-(p-methoxyphenyl)- 2-phenyl-	trans	7

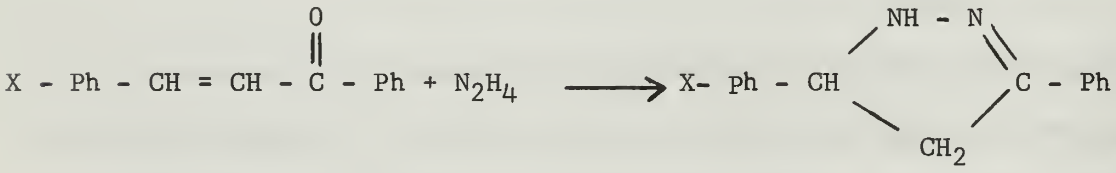
TABLE VI

The method of choice for the synthesis of all the 1, 2 diarylcyclopropanes prepared was the base catalyzed decomposition of 2-pyrazolines (51). All of the prerequisite, 1, 3-diarylpropenones (XXVIII) (chalcones) were prepared by base condensation of acetophenone (XXVII) with benzaldehyde. The addition of hydrazine to the chalcone resulted in the 2-pyrazoline (XXIX). Various catalysts for the decomposition of diaryl-2-pyrazolines at elevated temperatures have been used.



$$X - Ph - CHO + CH_3 - \overset{O}{\overset{\|}{C}} - Ph \xrightarrow[ETOH]{OH^-} X - Ph - CH = CH - \overset{O}{\overset{\|}{C}} - Ph$$

XXVII XXVIII



XXVIII XXIX

These include platinized asbestos (51), potassium hydroxide with copper-bronze (52) and large amounts of powdered potassium hydroxide (46). In this study smooth decompositions were obtained using less than 0.1 g of powdered potassium hydroxide. When this amount of base was used it was possible to distill the resulting isomeric mixture of cyclopropanes without extraction to remove the excess KOH. Some alkyl-2-pyrazolines have been decomposed in the absence of any basic catalyst (46). This was attempted in this study but no decomposition of 3-phenyl-5-(p-methoxyphenyl)-2-pyrazoline was observed on heating to 260°C. The pyrazoline did however decompose readily at 215°C in the presence of a trace of powdered KOH.[1] The overall yields[2] of cyclopropanes obtained by this method varied from 30-50% for the isomeric mixtures. The amount of cis isomer obtained was in all cases less than the amount of trans isomer.

Several of the cyclopropanes prepared have not been previously reported and were characterized by their infrared, ultraviolet and proton magnetic resonance spectra. The infrared spectrum of each of the isomers prepared is recorded in Appendix I. Various features of the infrared spectrum of cyclopropanes have been described as being "characteristic" of cyclopropanes (3,6). In the following paragraphs some of these features in addition to others are discussed in relation to these spectra.

The region from 3100-3000 cm^{-1} in all of the spectra has the same general appearance. Two predominant bands at 3060 cm^{-1} and 3030-3020 cm^{-1} are observed in all spectra. In general the band at 3030-20 cm^{-1} is of higher intensity and shifts to lower energy (5 cm^{-1}) when going from the trans to cis isomer of a particular compound. Several shoulders are also evident in all of the spectra. These are at 3110 cm^{-1} to 3000 cm^{-1}. This region is obviously complicated by the presence of both the cyclopropyl and aromatic C-H stretch absorbances. The infrared spectra of cis-and trans-1, 3-diphenylpropene also show nearly this same pattern at the same frequencies in this region from 3100-3000 cm^{-1}.

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[1] See the Historical Section Part I for a discussion of the mechanism of the decomposition of 1-and 2-pyrazolines.

[2] Based on starting materials of acetophenone and the substituted benzaldehyde.

The region below 3000 cm^{-1} in the aliphatic C-H stretch is devoid of any absorption for all of the cyclopropanes with the exception of $-CH_3$ absorptions in the p-methoxy and p-methyl compounds. In comparison cis-and trans-1, 3-diphenylpropene have methylene absorptions at 2895 cm^{-1} and 2835-30 cm^{-1}. From this region alone then it can be seen that most cyclopropanes that have aromatic substitutents only are readily identifiable by this portion of the spectrum. This is especially true when attempting to discern between the cyclopropane and the isomeric olefin.

Another frequency range often identified as the ring deformation mode is that from 1050 to 1000 cm^{-1}. Knipmeyer (52) observed a band for cis-1, 2-diphenylcyclopropane at 1017 cm^{-1} which is totally missing in the trans isomer. This same observation was made here for a band at 1010 cm^{-1} in cis-1, 2-diphenylcyclopropane which is missing in the trans isomer. Both isomers of the para-fluoro, para-chloro- and para-methyl compounds have an absorbtion within ± 5 cm^{-1} of 1010 cm^{-1}. However only the cis isomers of the meta-chloro- and para-methoxy have absorption here. In addition it should be noted that cis-1, 3-diphenylpropene shows a weak absorption at 1010 cm^{-1} while the trans isomer shows none. This region of the spectrum is complicated by aromatic C-H in plane deformation modes (6) as can be noted by the presence of a band at 1027 cm^{-1} in all of the spectra.

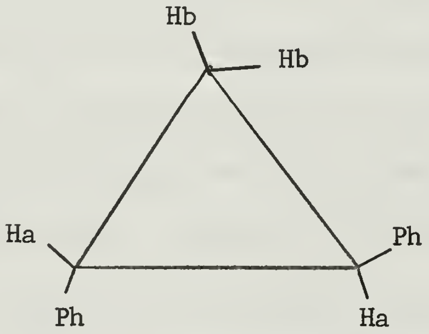
Numerous authors have also cited a band at 860 cm^{-1} in attempts to identify cyclopropanes using infrared spectroscopy (23,62). No significant absorptions in this vicinity were noted for any of these cyclopropanes.

Other diagnostic features however can be readily noted from an examination of these spectra which can be useful in identifying the compound as well as determining its geometric configurations. All of the trans isomers have a doublet at 1360-1375 cm^{-1} (± 5 cm^{-1}). None of the cis isomers have an absorption in this region nor does either isomer of 1,3-diphenylpropene. Knipmeyer (52) observed a band at 1204 cm^{-1} in cis-1, 2-diphenylcyclopropane which is absent in the trans isomer. In this study most of the cis isomers had an absorption within 5 cm^{-1} of 1195 cm^{-1}. However in cases where this band was present in the cis isomer a similar band of somewhat lower intensity was found at slightly higher frequencies, 1205 ± 5 cm^{-1}. Neither isomer of 1, 3-diphenylpropene absorbed in this region.

All of the trans isomers showed a doublet (separated by 10 cm^{-1}) between 730 and 760 cm^{-1}. In the cis isomers this doublet is not present. Two or more bands are present however between 700 and 800 cm^{-1} for the cis isomers but show a separation of greater than 20 cm^{-1} as compared to 10 cm^{-1} for the trans isomers. This feature was not observed in the spectrum of either cis-or trans-1, 3-diphenylpropene.

The cis isomers of all of the cyclopropanes showed a band of medium to low intensity at 610 ± 10 cm^{-1}. The trans isomers had no absorbtion in this portion of the spectrum. The isomers of 1, 3-diphenylpropene showed a similar feature. On the basis of these observations, it appears that 1, 2-diarylcyclopropanes can be identified and characterized on the basis of their infrared spectra. This is in contrast to other alkyl and aryl substituted cyclopropanes which cannot be characterized solely on the basis of their infrared spectra (109).

The proton magnetic resonance of the cyclopropanes proved to be the most diagnostic feature for the characterization of these compounds as well as the assignment of their geometric isomers. The N.M.R.[1] spectra of cis-and trans-1, 2-diphenylcyclopropane were identical with those previously published (73). A summary of these spectra is given in Table VII where the various protons can be distinguished by reference to XXX below.



XXX

That one can distinguish readily between substituted cyclopropanes and their corresponding olefins can be observed by a comparison of the spectra of cis-and trans-1, 3-diphenylpropene with cis-and trans-1, 2-diphenylcyclopropane.

Several general features of these spectra are worthy of comment. All of the methylene protons in both the cis and trans isomers appear as a multiplet (quartet) and lie within ± 0.06 ppm of 1.30 ppm. This resonance is unaffected by the configuration of the molecule and the type of substituent and is the same as that observed for an aliphatic methylene group (81). The benzylic protons appear as a multiplet (triplet) centered between 2.3 and 2.4 ppm for the trans isomers and 2.0 and 2.1 ppm for the cis isomers. The difference of 0.3 ppm between the cis

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[1] All values are given p.p.m. (δ).

TABLE VII*

Compound	Isomer	Ph-H	Ha	Hb	Other
p-H	cis	6.95	2.38	1.34	
	trans	7.05	2.08	1.30	
p-CH_3	cis	6.85	2.25	1.22	2.05
	trans	7.00	2.05	1.28	2.27
p-Cl	cis	7.00	2.32	1.36	
	trans	7.09	2.11	1.30	
p-OCH_3	cis	6.78	2.31	1.28	3.45
	trans	7.00	2.10	1.32	3.75
p-F	cis	6.90	2.31	1.30	
	trans	7.00	2.00	1.30	
m-Cl	cis	6.93	2.41	1.36	
	trans	7.05	2.00	1.30	

*Values in ppm (δ) from tetramethylsilane.

and *trans* isomers is generally accounted for on the basis of conformation difference of the phenyl rings (14) as well as the influence of the cyclopropane ring current (20). The aromatic proton absorption is shifted up field (from usual aromatic protons) in all cases to multiplets centered at 6.95 ± 0.05 ppm for the *cis* isomers and 7.00 ± 0.05 ppm for the *trans* isomers.

In general, the *trans* isomers have a more complex splitting than is observed for the *cis* isomers with respect to the aromatic protons. The differences in conformation between the *cis* and *trans* isomers readily accounts for these observations (14). In the *trans* isomers the lowest energy conformation is obtained when the planes of both phenyl rings are parallel to each other and perpendicular to the plane of the cyclopropane. In this orientation one of the ortho protons lies directly over the cyclopropane ring. The other ortho proton lies external to the influence of the cyclopropane ring. However the barrier to rotation of the phenyl ring in the absence of ortho substituents is small and the two ortho protons are indistinguishable. As the temperature is lowered, studies (14) have shown that the ortho protons in arylcyclopropanes experience an increase in shielding while the meta protons are relatively unaffected. Protons located in the plane of the cyclopropane ring experience a deshielding effect while protons located near the threefold axis of symmetry show a shielding effect. In contrast to the *trans* isomer the phenyl rings in the *cis* isomer are more restricted sterically in their rotation. In addition the *cis* phenyl rings are oriented (with respect to each other and the cyclopropane ring) differently than in the *trans* isomer. Curtin *et al.* (20) observed a "*cis* effect" in *cis*-diphenylcyclopentanone where the aromatic proton absorption was shifted (0.2 - 0.4 ppm) toward higher field with respect to the *trans* isomer. Presumably this is the result of the mutual influence of the ring current in each phenyl ring. A similar shift was noted for cis-1, 2-diphenylcyclopropanes. All of the 1, 2-diarylcyclopropanes examined in this study showed a similar effect but the magnitude of the shift is slightly smaller (0.1-0.25 ppm).

In addition to the infrared and N.M.R. spectra, ultraviolet spectra were prepared on all of the cyclopropanes. All of the spectra have features similar to that of cis-and trans-1, 2-diphenylcyclopropane (52). The trans isomers all showed a maximum between 230-235 mμ with molar extinction coefficients of about 2 X 10^4. The cis isomers do not have a definite maximum but exhibit a shoulder at about 220 mμ with a corresponding molar extinction coefficient of 1.3 X 10^4. The conformations of the cis and trans isomers (discussed above) are also applicable to an explanation of the ultraviolet spectral results. In the trans isomer the lowest energy conformation of the phenyl rings permits orbital overlap between the phenyl rings and the heavily p-weighted (75a), partially delocalized orbitals of the cyclopropane ring. On the other hand only the highest energy conformation of the cis isomer would permit significant conjugation between the cyclopropane bond and the pi system of the phenyl rings as it appears to exist in the trans isomer.

Reactions of 1, 2-Diarylcyclopropanes with Bromine in Carbon Tetrachloride

To further demonstrate the well developed analogy between cyclopropanes and olefins a series of experiments were conducted on the compounds prepared in this work. These reactions with bromine in carbon tetrachloride were carried out to (1) determine the extent, if any, of electrophilic addition of bromine to these cyclopropanes, (2) examine the kinetics of the photochemical addition of bromine, (3) determine the reaction products of these additions and (4) make a comparative rate study among the various compounds and determine the influence of the para substituents on these reactions.

Electrophilic cleavage of the cyclopropane ring in various compounds has been demonstrated by many workers. Cleavage of the ring has been demonstrated with halogen acids (55,58), lead tetra acetate (72), thallium acetate (71), mercuric acetate (60), and halogens (104). Most of these reactions have been carried out in either aqueous or polar media in the absence of light. In this study (Experimental Part II) the dark reactions of 1, 2-diarylcyclopropanes were carried out with bromine in carbon tetrachloride. Under the conditions of total darkness all of the cyclopropanes failed to react to any extent in 24 hours with the exception of 1-(p-methoxyphenyl)-2-phenyl-cyclopropane. Both isomers of this compound reacted to some extent under these conditions. This is in contrast to alkyl substituted cyclopropanes which do react with bromine under similar conditions (64). No attempt was made to determine the reaction products for the dark reactions of the para-methoxy compound. However, the thin layer chromatogram of the reaction mixture gave (after development) an identical appearance to the chromatogram from the photo induced reaction mixtures (to be considered below).

Prior to a study of the kinetics of the photochemical addition of bromine to these cyclopropanes it was necessary to demonstrate that not only was the dark (ionic) addition negligible under the reaction conditions but also that the reaction led to essentially only one product. To this end quantitative reactions of the cyclopropanes with bromine in carbon tetrachloride were carried out and the reaction products examined. The reaction of trans-1, 2-diphenlycyclopropane with bromine was carried out and the resulting reaction mixture analyzed using thin layer chromatography. Five separate bands were identifiable when this chromatogram was developed using formaldehyde (2%) in sulfuric acid.[1] Column chromatography with silica gel and alumina as well as preparative thin layer chromatography were used to isolate these reaction products. The major product, 1, 3-dibromo-1, 3-diphenylpropane, accounted for 85% of the starting material. Similar treatment of the other cyclopropanes showed that at least 80% of the starting material reacted to give the 1, 3-dibromo product in every case.

All attempts to isolate the other reaction products were unsuccessful. There are several salient points regarding these products which should be noted. In order to obtain sufficient quantities of these products, reactions were carried out in solutions more concentrated than those used in the kinetic runs. It was observed that as the concentrations increased the percentage of starting material recovered as the 1, 3-dibromo product decreased. Hence, for the kinetic determinations, where the concentrations were less by a factor of 10, the percentages of starting material reacting to give the 1, 3-dibromo product are a minimum figure. Several possible products from this reaction were eliminated on the basis of their independent preparation and comparison with reaction mixtures using thin layer chromatography. This will be considered in more detail below in a discussion of the mechanism of the reaction.

As indicated above the major reaction product obtained for all of the 1, 2-diarylcyclopropanes (XXXI) reacted was the 1, 3-dibromo-1, 3-diarylpropane (XXXII).

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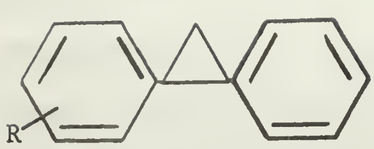
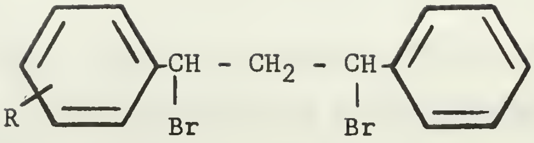
[1] Photographs of several thin layer chromatograms are presented in Appendix IV along with a discussion of these chromatograms.



XXXI

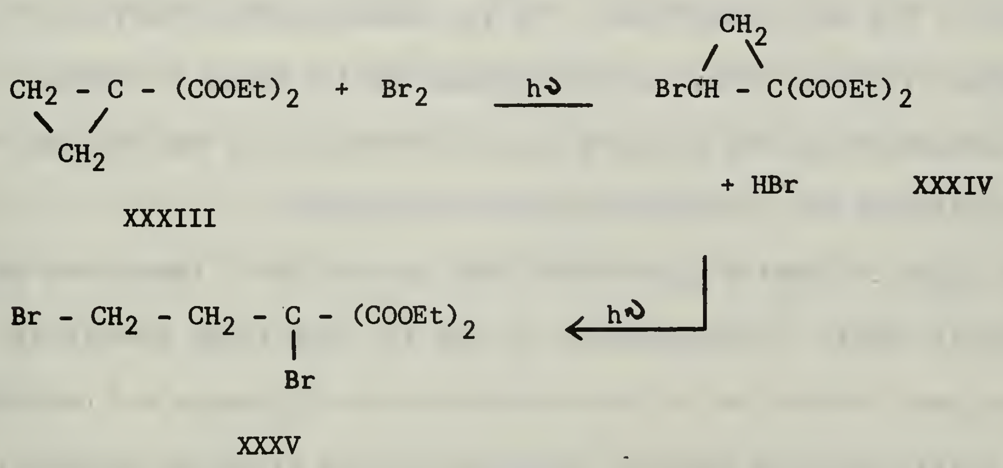


XXXII

Infrared spectra were prepared on all of these compounds as well as carbon-hydrogen-bromine analyses. Authentic samples of 1, 3-dibromo-1, 3-diphenylpropane and 1, 3 dibromo-1-(p-chlorophenyl)-3-phenylpropane were prepared by an independent route. The infrared spectra and N.M.R. spectra were identical to those obtained from the work up of reaction mixtures of the cyclopropanes. The 1, 3-dibromo reaction products from the other cyclopropanes were not identified by their counter synthesis but were identified on the basis of their infrared spectra, N.M.R. spectra and analyses.

The infrared spectra of these 1, 3-dibromo-1,3-diarylpropanes are reproduced in Appendix I. Some interesting features of these spectra are readily discernible especially when a comparison is made with the starting cyclopropane (6,67). A diffuse band in the aliphatic C-H stretch region from 2850 cm^{-1} to 3000 cm^{-1} can be seen in all of the spectra indicating the opening of the cyclopropane ring. The aromatic substitution region (2000 cm^{-1} to 1800 cm^{-1}) is the same in both the starting cyclopropane and the dibromo reaction product. In all of the dibromo reaction products several bands are present between 500-600 cm^{-1} which are assigned to the C-Br stretch (6). The N.M.R. spectra of the 1, 3-dibromo reaction products are recorded in Appendix II. The interpretation of these spectra is straightforward for the mixture of d,l and meso forms of these compounds.

The failure of these 1, 2-diarylcyclopropanes to react with bromine in CCl_4 in total darkness as well as the observed reactions taking place photochemically, clearly point to the radical nature of the ring cleavage. There are only a few instances of radical cleavage of cyclopropanes recorded in the literature. Nicolet and Sattler (68) carried out reactions of bromine with diethyl cyclopropane-1, 1-dicarboxylate (XXXIII). This reaction was considered in Part II of the historical introduction and is undoubtedly radical in nature. Their observations led them to suggest that the reaction proceeded first by substitution of bromine of XXXIII to give the 2-bromo derivative XXXIV. This was followed by splitting of the ring with the addition of the HBr (formed in the substitution) to give the aliphatic 1, 3-dibromo product (XXXV)



That this is not the mechanism here can be demonstrated by an examination of the reaction products one would expect from the presence of HBr in the system. In addition to cleavage of the substituted cyclopropane one would expect to find mono-bromo aliphatic compounds from the reaction of the cyclopropane with HBr. Other products resulting from cleavage between the most highly and least highly substituted carbons would also be expected in fair yields.

Other radical cleavages of cyclopropanes in bicyclic compounds have been observed (30,56) using N-bromosuccinimide. These also were considered in the historical introduction.

In order to discuss the conclusions which arose from this study of the photochemical ring cleavage of 1, 2-diarycyclopropanes, it is convenient to state the experimental results here. The reaction between bromine and 1, 2-diarylcyclopropanes proceeds smoothly in carbon tetrachloride when exposed to low intensities of light (between 320-450 mμ). One mole of bromine is consumed per mole of cyclopropane and the major product of the reaction is a 1, 3-dibromo-1,3-diarylpropane. At high concentrations (using stochiometric amounts of bromine and cyclopropane) the rate of the reaction tends toward zero order in cyclopropane and 3/2 order in bromine. In addition, at high concentrations, the rate is independent of the para-substituent. At low concentrations the rate of the reaction is first order in cyclopropane and 1/2 order in bromine. At low concentrations the relative rates of reaction for the various para-substituents fit a Hammett treatment of the data.

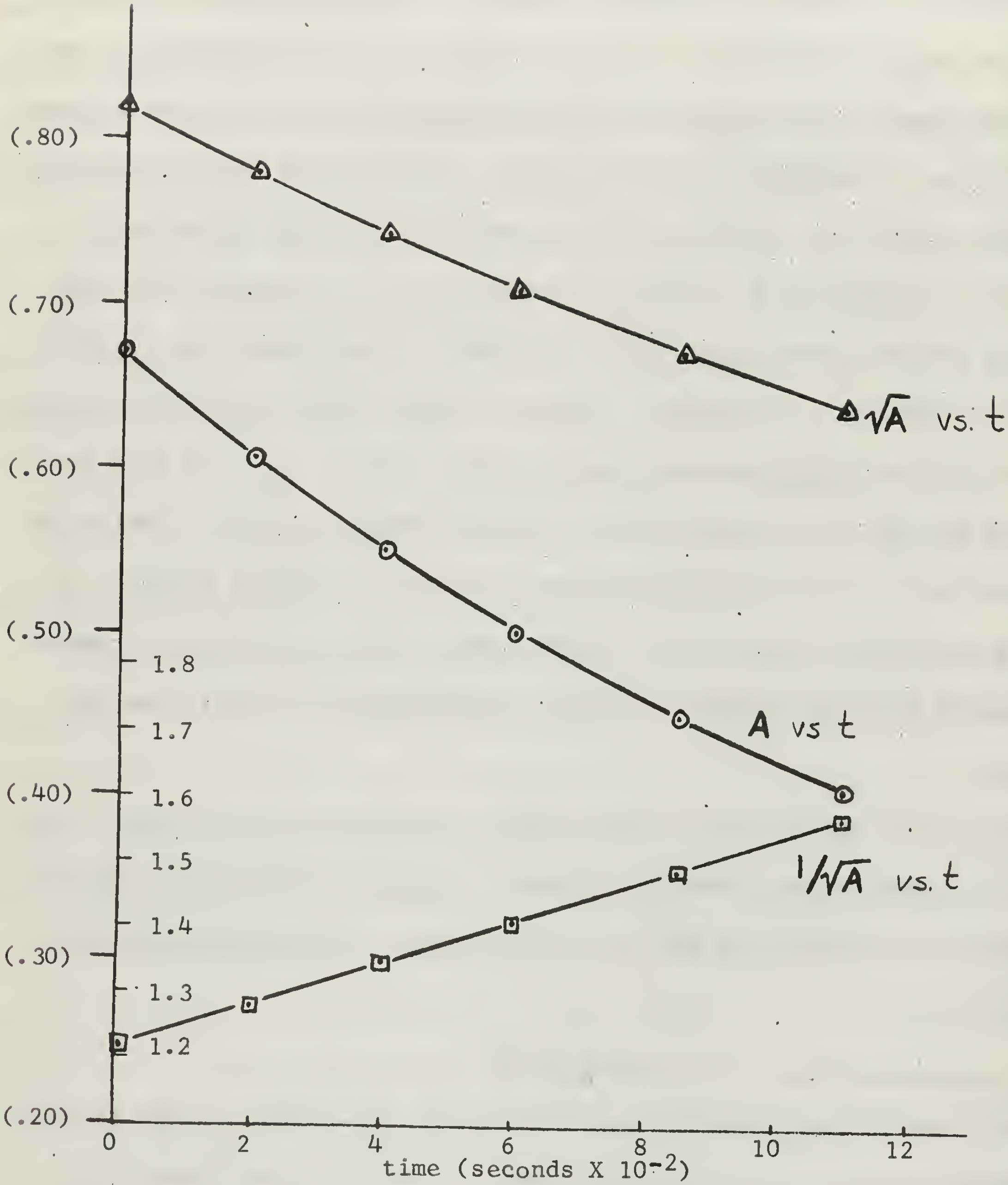
Two types of kinetic experiments were carried out. These have been described in detail in Experimental III and IV. The first kinetic experiments were carried out at low concentrations of bromine and cyclopropane to obtain relative rates of reactions for the different compounds. Considerable data were obtained for both the cis and trans isomers of the 1, 2-diarylcyclopropanes and is recorded in Appendix III. That the rate of reaction is dependent on the concentration of the cyclopropane as well as the para-substituent is readily apparent. When equimolar amounts of bromine and cyclopropane were reacted by exposure to low intensities of light the overall rate of the reaction was observed to be 3/2. As an example several functions of absorbance versus time are plotted in figure 2.

The kinetic runs were carried out such that only one variable was present within each run, that being the para-substituent. For each run the concentrations of the various cyclopropanes were kept as nearly equal as possible. The same carbon tetrachloride solution of bromine was used to dilute each sample to eliminate effects of dissolved oxygen on the relative rates of reaction. For runs in which the concentration of bromine was equal to the concentration of cyclopropane the data was treated by plotting $(\text{Absorbance})^{-\frac{1}{2}}$ against time. This was done for each reaction vessel in each run. In this manner a series of straight lines were obtained. By comparing the slopes of each line to the slope of the line for the unsubstituted compound (1, 2-diphenylcyclopropane) the relative rates of reaction are obtained. Figure 3 shows the data plot from Kinetic Run #37 for the trans compounds while figure 4 shows the data plot from Kinetic Run #44 for the cis series. Several runs were made in which the concentration of the cyclopropane was present in a tenfold excess. The data was plotted to obtain the pseudo-order of the reaction with respect to bromine for each compound. Plots of $(\text{Absorbance})^{\frac{1}{2}}$ versus time were linear.

The data obtained from these kinetic experiments weretreated in two ways to determine the extent of a Hammett sigma-rho correlation between the rates of reaction and the para-substituent. The Hammett relationship is

$$\log\left(\frac{k}{k_0}\right) = \sigma\rho$$

For this case k/k_0 is the ratio obtained from the slopes in each kinetic run where k_0 is for no substituent (para-H) and k for the substituted compound. The sigma values used are those tabulated by Jaffe (44). Using a least squares fit the following values were obtained. For the



Kinetic Run #44 trans 1,2-diphenylcyclopropane

Figure 2

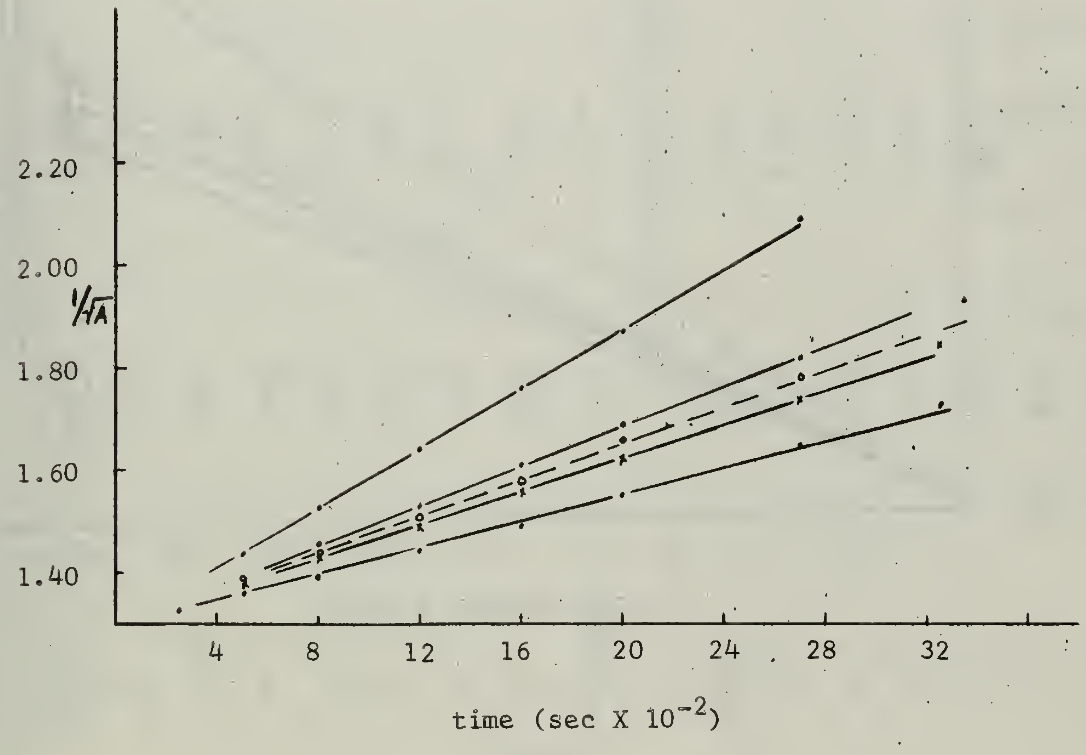


Figure 3

Kinetic Run #44

Slopes (1) 3.20
(2) 2.35
(3) 3.30
(4) 2.30
(5) 2.10
(6) 2.60

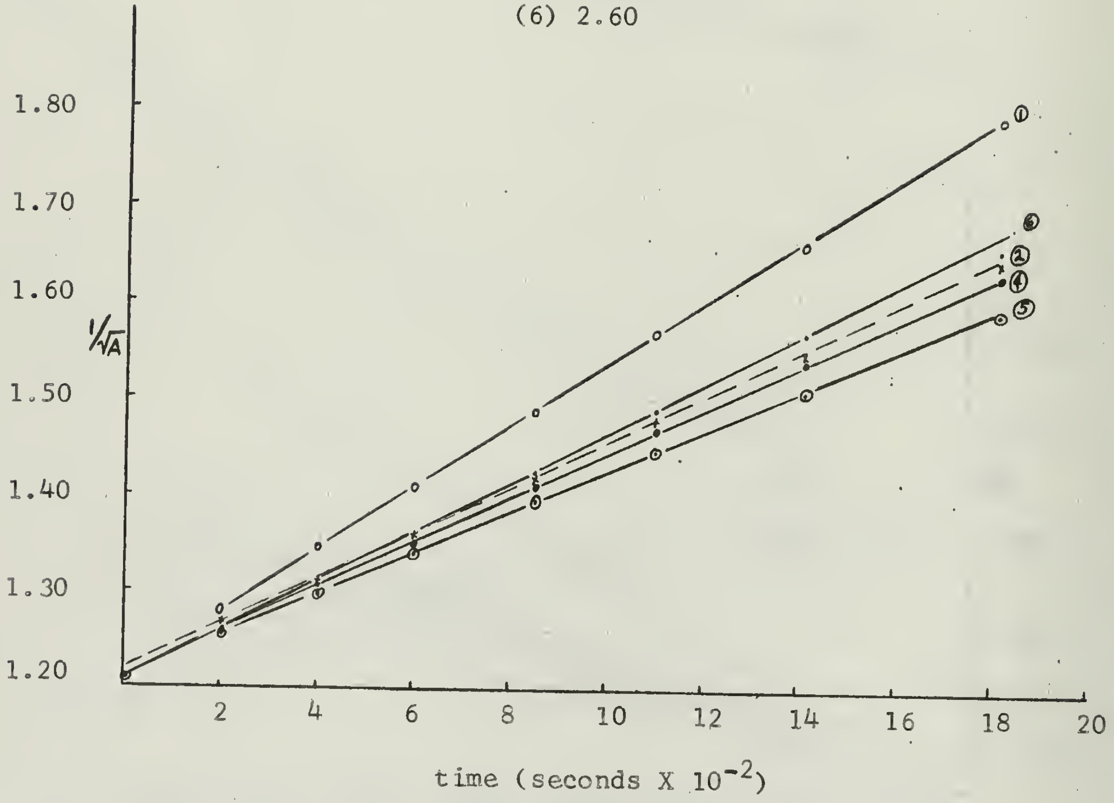


Figure 4

Table VIII

Corrected Relative Rates for Cis Compounds

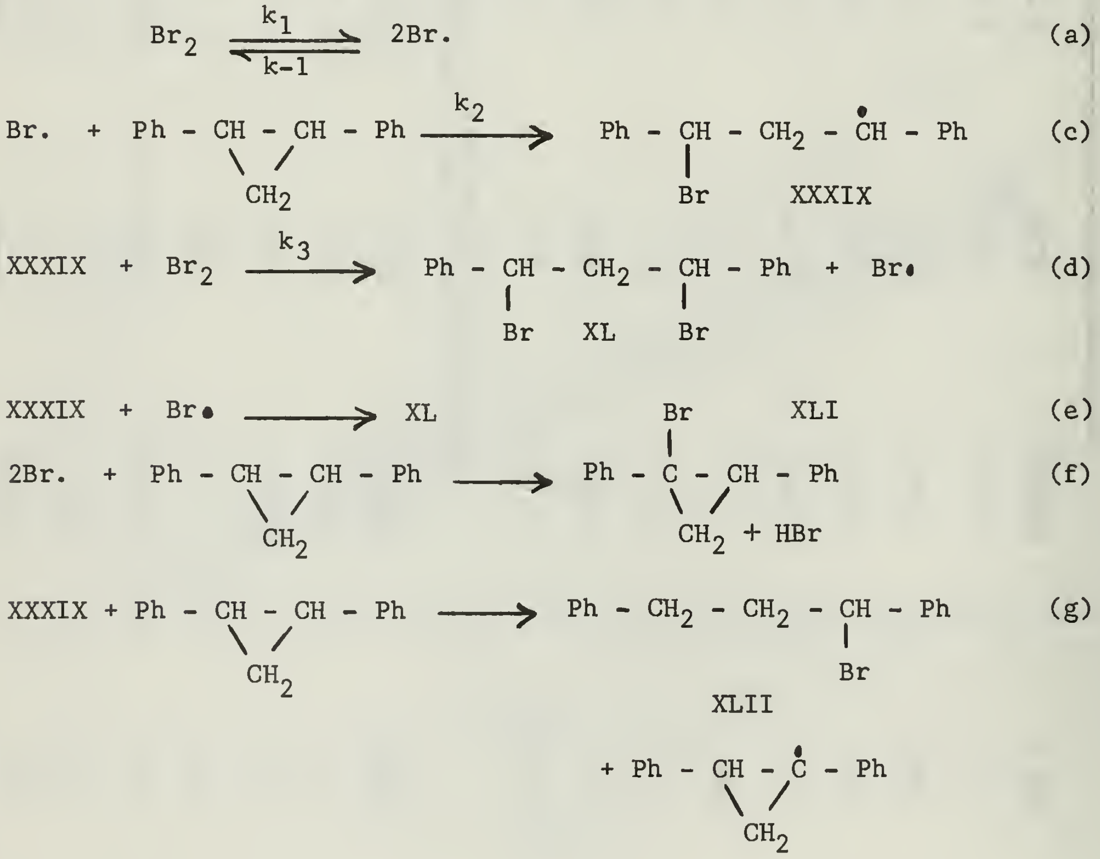
Run #	para-H	m-Cl	p-Cl	p-F	p-CH_3O
45	1.00	0.61	0.81	0.87	1.34
45a	1.00	0.67	0.75	0.96	1.34
44	1.00	0.83	0.85	0.90	1.24
41	1.00	0.68	0.78	-	1.80
40	1.00	0.83	0.91	-	1.39
39	1.00	0.78	0.80	-	1.45
38	1.00	0.77	0.86	-	1.23
Average	1.00	0.74	0.82	0.91	1.40

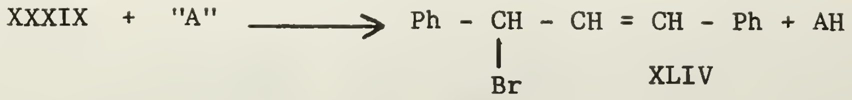
Corrected Relative Rates for Trans Compounds

Run #	para-H	m-Cl	p-Cl	p-F	p-CH_3O
37	1.00	0.66	0.88	0.95	1.60
36	1.00	0.72	0.87	0.94	1.40
35	1.00	0.60	0.78	0.92	1.32
34	1.00	0.65	0.87	0.90	1.20
29	1.00	-	0.91	-	1.21
28	1.00	-	0.79	-	1.74
Average	1.00	0.66	0.85	0.93	1.41

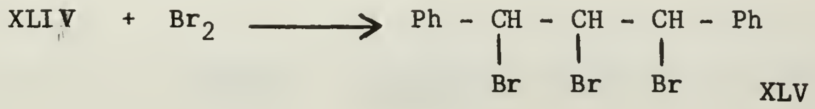
trans compounds rho = -.36 (s = 0.10 and r = 0.91). For the cis compounds rho = -0.47 (s = 0.11, r = .90), (44). Using simple averages of all the values obtained for the relative rates for each compound and plotting on semi-log paper (figure 5) the following values were obtained. For the cis compounds rho = -0.49 and rho = -0.44 for the trans compounds (Table VIII). Poor correlations of the data are obtained when sigma + values (9) are used. The Hammett correlation and the rho values obtained are reasonable for this type of reaction when compared to other free radical reactions.

Knowing the form of the rate equation, the nature of the product of the reaction and the rho value from the Hammett relationship, a mechanism utilizing the following equations can be formulated.


Br2 ⇌ 2Br. (k1, k-1) (a)
Br. + Ph - CH - CH - Ph (CH2) → Ph - CH(Br) - CH2 - ĊH - Ph XXXIX (k2) (c)
XXXIX + Br2 → Ph - CH(Br) - CH2 - CH(Br) - Ph XL + Br• (k3) (d)
XXXIX + Br• → XL (e)
2Br. + Ph - CH - CH - Ph (CH2) → Ph - C(Br) - CH - Ph (CH2) XLI + HBr (f)
XXXIX + Ph - CH - CH - Ph (CH2) → Ph - CH2 - CH2 - CH(Br) - Ph XLII + Ph - CH - Ċ - Ph (CH2) (g)



$$\text{XXXIX} + \text{"A"} \longrightarrow \text{Ph} - \underset{\substack{|\\ \text{Br}}}{\text{CH}} - \text{CH} = \underset{\text{XLIV}}{\text{CH}} - \text{Ph} + \text{AH} \qquad \text{(h)}$$



$$\text{XLIV} + \text{Br}_2 \longrightarrow \text{Ph} - \underset{\substack{|\\ \text{Br}}}{\text{CH}} - \underset{\substack{|\\ \text{Br}}}{\text{CH}} - \underset{\substack{|\\ \text{Br}}}{\text{CH}} - \text{Ph} \quad \text{XLV} \qquad \text{(i)}$$

The data for the dark reactions of these cyclopropanes eliminated the possibility of any serious competition between an ionic electrophilic addition and the observed radical addition. Using (c) above as the rate determining step in this sequence the rate equation becomes

$$\text{rate} = k' \text{(C) (Br.)} \qquad \text{where (C)} = \text{(cyclopropane)} \qquad \text{(j)}$$

Under the conditions of illumination employed $(\text{Br}\bullet)$ is related to (Br_2) from (a) by (k).

$$\text{Keq} = \frac{(\text{Br}\bullet)^2}{(\text{Br}_2)} \;;\; (\text{Br}\bullet) = (\text{Keq})^{\frac{1}{2}} (\text{Br}_2)^{\frac{1}{2}} \qquad \text{(k)}$$

Applying this substitution to the rate equation (j), (l) is obtained.

$$\text{rate} = k'' \text{(C)} \; (\text{Br}_2)^{\frac{1}{2}} \qquad \text{(l)}$$

When the concentration of C becomes large in (l) the rate equation becomes pseudo ½ order in bromine.

$$\text{rate} = k''' (\text{Br}_2)^{\frac{1}{2}}; \text{ where } k''' = k'' \text{(C)} \qquad \text{(m)}$$

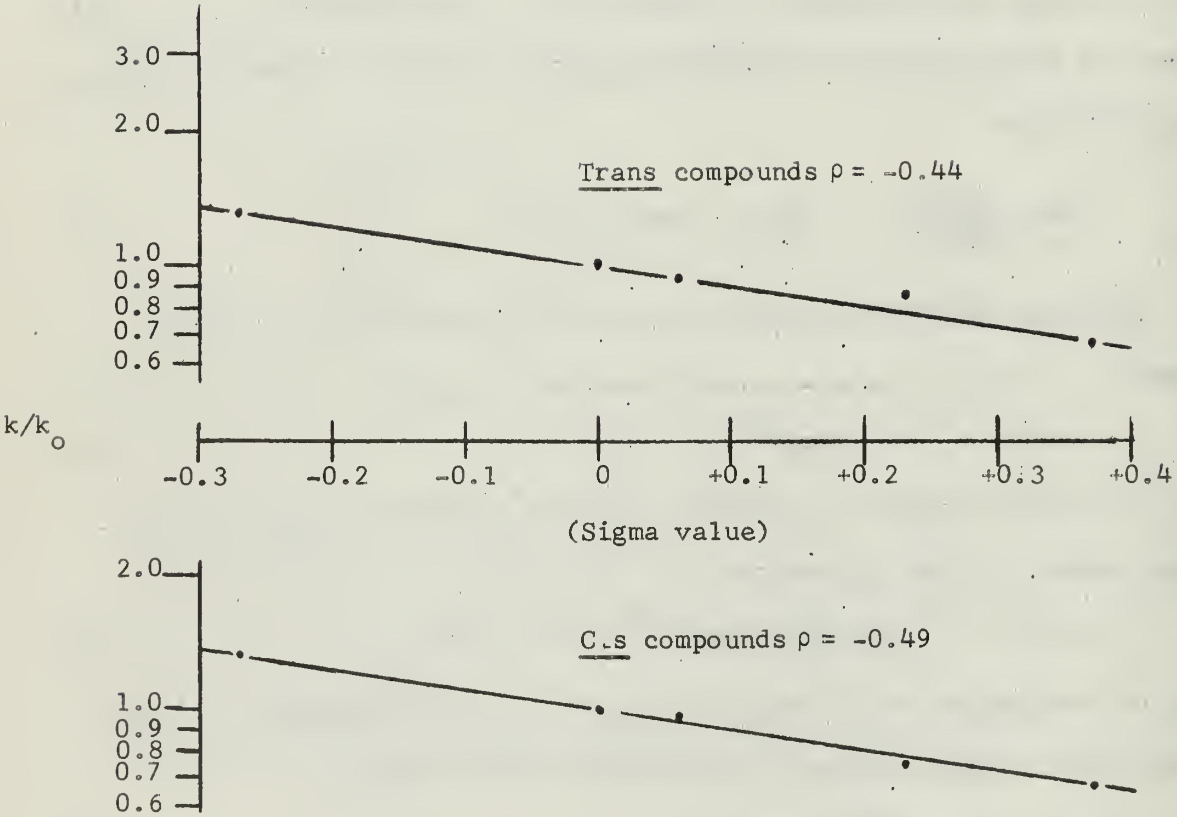
When the concentration of bromine is equal to the concentration of the cyclopropane, the stochiometry permits the substitution of

$$(\text{Br}_2) = \text{(cyclopropane)} \qquad \text{(n)}$$

and in this case the rate equation becomes

$$\text{rate} = k' \; (\text{Br}_2) \; (\text{Br}_2)^{\frac{1}{2}} = k' \; (\text{Br}_2)^{3/2} \qquad \text{(o)}$$

Using the rate of disappearance of bromine as a measure of the rate of



Hammett plots for relative reaction rates for *cis* and *trans* isomers of 1,2-diarylcyclopropanes

Figure 5

the reaction and integrating, (p) is obtained.

$$\int \frac{-d\,(Br_2)}{dt} = \int k''\,(Br_2)^{3/2}$$

$$\frac{1}{\sqrt{(Br_2)}} = \frac{1}{\sqrt{(Br_2)_o}} + k_{3/2}\,t \qquad \text{(p)}$$

Since the concentration of bromine was determined using spectrophotometric methods, absorbance (A) is directly proportional to the concentration. Making this substitution and ignoring the proportionality constant (since all of the rates determined are relative to the para-H compound), (q) is obtained.

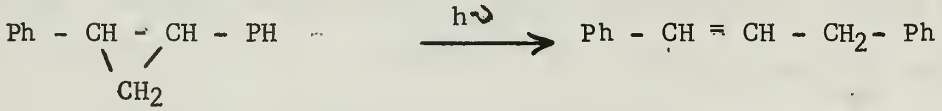
$$\frac{1}{\sqrt{A}} \propto kt \qquad \text{(q)}$$

Studies have been made (39) in which Hammett sigma-rho correlations have been found for benzylic hydrogen substitution by atomic bromine. In these studies the proton abstraction step (attack by Br·) is not the rate determining step. The rate determining step is the decomposition or reaction of the resulting benzylic radical to products. The stability of this radical is influenced by para substituents such that negative values for rho are obtained. This could also be the case here if equations (d) and/or (e) were the rate determining step. However if these were the rate determining steps the rate equation would necessarily be between 2 and 2.5 order overall depending on whether (d) or (e) predominates.

That (d) and/or (e) are the predominate steps following the rate determining step (c) can be seen from the major products obtained, the 1, 3-dibromo compounds. Kuivila _et al._ (as discussed above) obtained a dibromo product from the ring cleavage of a 1, 2- disubstituted cyclopropane using N-bromosuccinimide. If the ring is cleaved by a bromine radical in that case also, then the resultant radical must react either with another bromine radical or, as Roberts (81) suggests, a bromine molecule.

The reactions (f) through (i) may be eliminated as significant contributors to the overall reaction. The presence of these compounds was neither proven nor disproven. The occasional presence of HBr in some of concentrated reactions indicated (f) may be operative to a small extent. A light pink color observed for the band in the development of some of the thin layer chromatograms indicates possible aromatic substitution. Parabromo substituted aromatic compounds have been reported (6a) to give a pink color test with this same reagent. Other possibilities, however, have been eliminated in several ways.

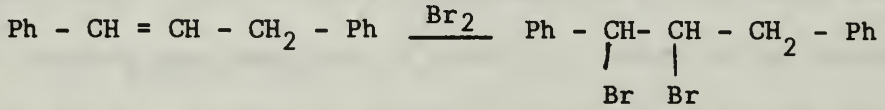
The isomerization of 1, 2-diarylcyclopropanes has been examined under several conditions. Griffin _et al._ (34a) have reported the isomerization of _cis_-1, 2-diphenylcyclopropane to the _trans_ compound as well as 1, 3-diphenylpropene (XLIV) and other products. These reactions were carried out in benzene and cyclohexane solutions under the influence of 253.7 mμ light at 40°.



XLIV

The reverse reaction was also demonstrated starting with pure XLIV. The geometric isomerization of 1, 2-diarylcyclopropanes has also been demonstrated thermally (84). Bell (5) has studied the triplet state of 1, 2-dimethylcyclopropane in an examination of its benzene and toluene photosensitized isomerization. That none of these isomerizations were occurring under the conditions of photolysis was demonstrated in the following manner. Solutions of the cyclopropanes in carbon tetrachloride were subjected to the identical conditions of irradiation as used in the kinetic runs. Analysis using g.p.c. before and after photolysis indicated no change in the solutions.[1]

Another distinct possibility was the bromine atom sensitized isomerization of the cyclopropanes. Isomerizations of olefins (107) has been demonstrated using atomic bromine as a catalyst. If such were the case here the dibromo-addition adduct (XLV) of XLIV would be expected as a reaction product. This dibromo product (XLV) was prepared by an independent synthesis. No evidence for its presence in the reaction mixture was found using thin layer chromatography and infrared spectroscopy.



$$\mathrm{Ph-CH=CH-CH_2-Ph} \xrightarrow{Br_2} \mathrm{Ph-\underset{Br}{CH}-\underset{Br}{CH}-CH_2-Ph}$$

XLIV XLV

The second type of kinetic experiment was carried out in the flow system as described in Experimental Part IV.

In using a flow system which included an infrared spectrophotometer as well as a U.V. spectrophotometer, it was hoped to obtain additional information regarding the rate equation of this reaction. The rate of disappearance of bromine was measured in the visible, while the rate of product appearance was to be measured in the infrared. In CCl_4 only one "window" was available where a new infrared absorption appeared after the reaction of bromine and cyclopropane. This was the C-H (2850-2950 cm^{-1}) absorption which is present when the cyclopropane ring is cleaved to give the 1, 3-diaryl-aliphatic compound. In the few runs that infrared data was obtained it was possible to observe the aliphatic C-H band "grow" during the course of the reaction while some decrease in intensity was observed for the overlapping cyclopropyl and aromatic C-H stretch frequencies. No quantitative information was obtained from the infrared measurements due to (1) the proximity of the bands considered above and the inability to resolve them, and (2) the polychromatic radiation of the infrared spectrophotometer causing photolysis of the reaction mixture in the flow cell.

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[1] That the incident light was of 320 mμ or greater was also discussed in the Experimental. The failure of malachite green leucocyanide (a dye sensitive to light of 310 mμ and below) to undergo decomposition under the conditions of photolysis was shown.

The remainder of the kinetic runs made using the flow system omitted the infrared spectrophotometer. Although no conclusive determination of the rate equation can be ascertained from the data[1] from these runs, some inferences can be drawn. The data in each case was plotted to determine the order of the reaction with respect to bromine. In all cases the order was determined to be 3/2. No correlations of the data were obtained for 5/2, 1/2, 1 or 0 order dependence in bromine (see figure 2). In contrast to the kinetics at low concentrations the rate of reaction at higher concentrations (0.05 - 0.10 molar) was insensitive to the concentration and the substitution of the 1, 2-diarylcyclopropanes used. The data in all cases however did fit the rate equation

$$\text{rate} = k' \, (Br_2)^{3/2}.$$

This same type of observation has been made on similar photobromination reactions. Rondestvedt et al. (85) examined the photobromination of 2-phenylethen-1-sulfonyl chloride (XXXVI). In concentrations of 0.05 molar the reaction was independent of the concentration of XXXVI and 3/2

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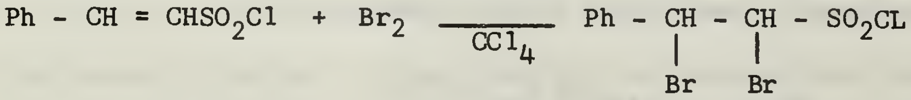
[1] The reproducibility of the data at these higher concentrations in this flow system was poor. A number of reasons for this behavior are possible. Photochemical brominations of olefins in solution is complicated by the presence of dissolved oxygen (4,107). Temperature control was difficult to maintain in the flow system, and a reliable and convenient chemical actinometer is not available (for the portion of the visible spectrum used) to measure the intensity of the incident light.



$$Ph-CH=CHSO_2Cl + Br_2 \xrightarrow[CCl_4]{} Ph-\underset{Br}{CH}-\underset{Br}{CH}-SO_2CL$$

XXXVI XXXVII

in bromine. Under conditions of low illumination the product obtained was the 1, 2 dibromo-compound (XXXVII). Bertland and Nicolet (6b) had made a similar observation earlier with the photobromination of α-phenylcinnamonitrile. The following equations will be used to discuss these observations.

$$Br_2 \rightleftharpoons 2Br\bullet \qquad (q)$$

$$Br\bullet + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_3\bullet \qquad (r)$$

$$Br_3\bullet + (\text{cyclopropane}) \xrightarrow{k_2} \text{products} \qquad (s)$$

By applying the steady state approximation to ($Br_3\bullet$), (t) is obtained.

$$(Br_3\bullet) = \frac{k_1(Br\cdot)(Br_2)}{k_{-1} + k_2(C)} \qquad (t)$$

where (C) = (cyclopropane)

Imposing the equilibrium condition of (a) on this expression yields (u).

$$(Br_3\bullet) = \frac{k_1(Keq)^{\frac{1}{2}}(Br_2)^{3/2}}{k_{-1} + k_2(C)} \qquad (u)$$

Since the slow step is (s) when the steady state approximation is applied to ($Br_3\bullet$), the rate of the reaction is given by (v).

$$\text{rate} = k_3(Br_3\bullet)\ (C) \qquad (v)$$

Using the value of ($Br_3\bullet$) from (u) above, (w) is obtained.

$$\text{rate} = \frac{k_1 k_2 (Keq)^{\frac{1}{2}} (Br_2)^{3/2} (C)}{k_{-1} + k_2 (C)} \qquad (w)$$

If k_2 and k_{-1} are of the same order of magnitude and the concentration of the cyclopropane is relatively high (w) reduces to

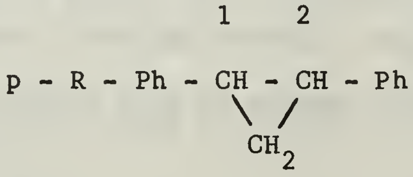
$$\text{rate} = k_1 \, (keq)^{\frac{1}{2}} \, (Br_2)^{3/2} \qquad (x)$$

Hence, in spite of the fact that the slow step, (s), involves the cyclopropane, no dependence on its concentration is noted in the rate expression.

As shown above for low concentrations (less than 0.005 molar) the rate of the reaction is first order in cyclopropane. The equilibrium concentration of $(Br_3\bullet)$ is dependent on $(Br_2)^{3/2}$. Hence the concentration of $(Br_3\bullet)$ is markedly affected by changes in the concentration of Br_2. At low concentrations of Br_2 then the low concentration of $Br_3\bullet$ with respect to $Br\bullet$ allows the competitive reaction of $Br\bullet$ with the cyclopropane to predominate.

It is readily apparent that some radical chain effects should be noted for this type of reaction if equation (d) above appears equally or more likely than (c). Quantum yield determinations were carried out on reaction mixtures of trans-1, 2-diphenylcyclopropane. The reaction conditions were similar to those used for the kinetic experiments. At low concentrations of bromine and cyclopropane the quantum yield was 2. As the concentrations were increased the quantum yield also increased. A quantum yield of 7 was obtained for concentrations of approximately 0.02 molar in bromine and cyclopropane. It would be expected that equation (d) above would become more prevalent as the concentration of bromine increased. Equation (d) is a chain propagator and an increase in the average chain length and quantum yield are observed.

On the basis of the data obtained it is not possible to identify the site of attack of the bromine radical at any concentration. That is, for the compounds which have a para substituent, does the bromine radical attack the benzylic carbon (1 below) of the substituted ring in preference to the benzylic carbon (2 below) having the unsubstituted phenyl ring. If the unsubstituted carbon is attacked the resulting aliphatic



$$p - R - Ph - \underset{\substack{\diagdown\ \diagup \\ CH_2}}{\overset{1}{CH} - \overset{2}{CH}} - Ph$$

compound is a benzylic radical stabilized by the para substituents. On the other hand since bromine radicals are electrophilic in nature, the benzylic carbon having the highest electron density might be favored for initial attack.

SUMMARY

This work was undertaken to pursue further the already well established analogy between cyclopropanes and olefins. The analogy has been studied with respect to spectral properties as well as reactions. During this work a series of 1,2-diarylcyclopropanes were prepared some of which have not previously been reported in the literature. These compounds were characterized by their infrared spectra, ultraviolet spectra and nuclear magnetic resonance spectra as well as the conventional physical constants.

Reactions of these compounds with bromine in carbon tetrachloride were studied under dark and photolytic conditions at room temperature. Under dark conditions no significant reactions were observed for any of the cyclopropanes. Under photochemical conditions (visible light) the cyclopropanes were found to react with equi-molar amounts of bromine to give ring cleavage products, the 1,3-dibromo-1,3-diaryl-compounds.

The kinetics of these reactions were studied and the rates of reaction for each para-substituted 1,2-diarylcyclopropane determined relative to 1,2-diphenylcyclopropane. The reaction rates plotted against Hammett sigma values gave linear plots for both cis and trans isomers. For the cis isomers $\rho = -.49$ and for the trans isomers $\rho = -.44$.

The rate equation at low concentrations (0.003 molar) was found to be

$$\text{rate} = k(\text{cyclopropane})(Br_2)^{\frac{1}{2}}.$$

A mechanism for this reaction has been proposed in which the rate determining step is the attack of atomic bromine on the 1-2, carbon-carbon bond.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to his research director, Dr. Charles F. Rowell, for his patient encouragement and support.

The author also wishes to express his gratitude to the United States Navy for the opportunity to attend this institution and perform this research.

Many discussions with Dr. John W. Schultz were most helpful--for this the author is grateful.

Thanks are also due to Mr. Peter Savo and Mr. Tom Burson for their technical assistance. The help of Mr. Donald W. Moore in obtaining proton magnetic resonance spectra is also gratefully acknowledged.

The author would also like to express his appreciation to Dr. Carlos P. Cardenas, Miss Georgia Lyke and Mr. Robert G. Hazzard.

To his parents, Mr. and Mrs. Thomas J. Hoffmann, his wife Rachael, and to his children, Karen, Sarah, Raymond, Harold, and Donald, this dissertation is dedicated.

Appendix I

APPENDIX I

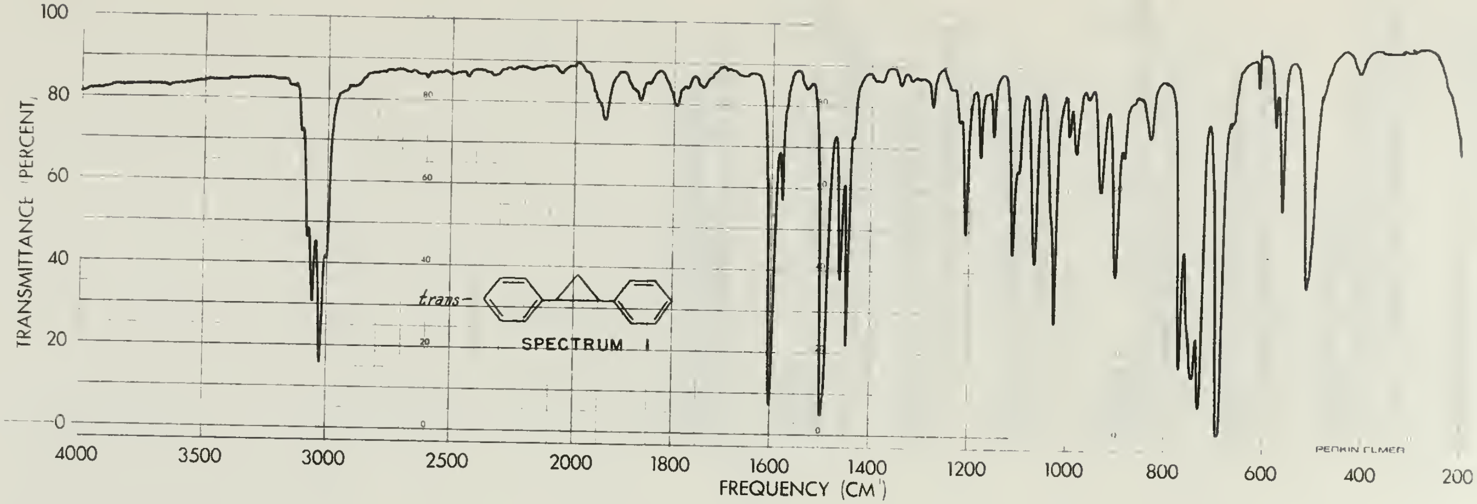
The infrared spectra recorded in this Appendix were recorded on a Perkin-Elmer Model 621 double beam spectrophotometer. Liquids were done neat between cesium iodide discs using a 0.015 mm (nominal) spacer unless otherwise indicated. The spectra of solids were obtained using potassium bromide pellets.

The table of contents for this Appendix and Appendix II is given on the following pages.

Table of Contents for Appendices I and II

NMR Spectrum # Appendix II	IR Spectrum # Appendix I	Compound
1	1	dl-*trans*-1, 2-diphenylcyclopropane
2	2	*cis*-1, 2-diphenylcyclopropane
3	3	d,l-*trans*-1-(p-methylphenyl)-2-phenylcyclopropane
4	4	*cis*-1-(p-methylphenyl)-2-phenylcyclopropane
5	5	*cis*-1-(p-chlorophenyl)-2-phenylcyclopropane
6	6	d,l-*trans*-1-(p-chlorophenyl)-2-phenylcyclopropane
7	7	*cis*-1-(m-chlorophenyl)-2-phenylcyclopropane
8	8	d,l-*trans*-1-(m-chlorophenyl)-2-phenylcyclopropane
9	9	*cis*-1-(p-fluorophenyl)-2-phenylcyclopropane
10	10	d,l-*trans*-1-(p-fluorophenyl)-2-phenylcyclopropane
11	11	d,l-*trans*-1-(p-methoxyphenyl)-2-phenylcyclopropane
12	12	*cis*-1-(p-methoxyphenyl)-2-phenylcyclopropane
13	13	d,l-*trans*-1-(p-dimethylamino-phenyl)-2-phenylcyclopropane
14	14	*cis*-1, 3-diphenylpropene
15	15	*trans*-1, 3-diphenylpropene
16	16	1, 2-dibromo-1, 3-diphenylpropane
17	17	1, 3-dibromo-1, 3-diphenylpropane

NMR Spectrum # Appendix II	IR Spectrum # Appendix I	Compound
18	18	1, 3-dibromo-1, 3-diphenylpropane (from diol)
	19	Minor reaction product from 1, 2-diphenylcyclopropane plus bromine in CCl_4.
	20	1, 3-dibromo-1-(p-chlorophenyl)-3-phenylpropane.
	21	1, 3-dibromo-1-(p-chlorophenyl)-3-phenylpropane (from diol)
19	22	1, 3-dibromo-1-(p-fluorophenyl)-3-phenylpropane
	23	1, 3-dibromo-1-(p-methoxyphenyl)-3-phenylpropane
20	24	1, 3-dibromo-1-(p-methoxyphenyl)-3-phenylpropane (from diol)
21	25	1, 3-dibromo-1-(m-chlorophenyl)-3-phenylpropane



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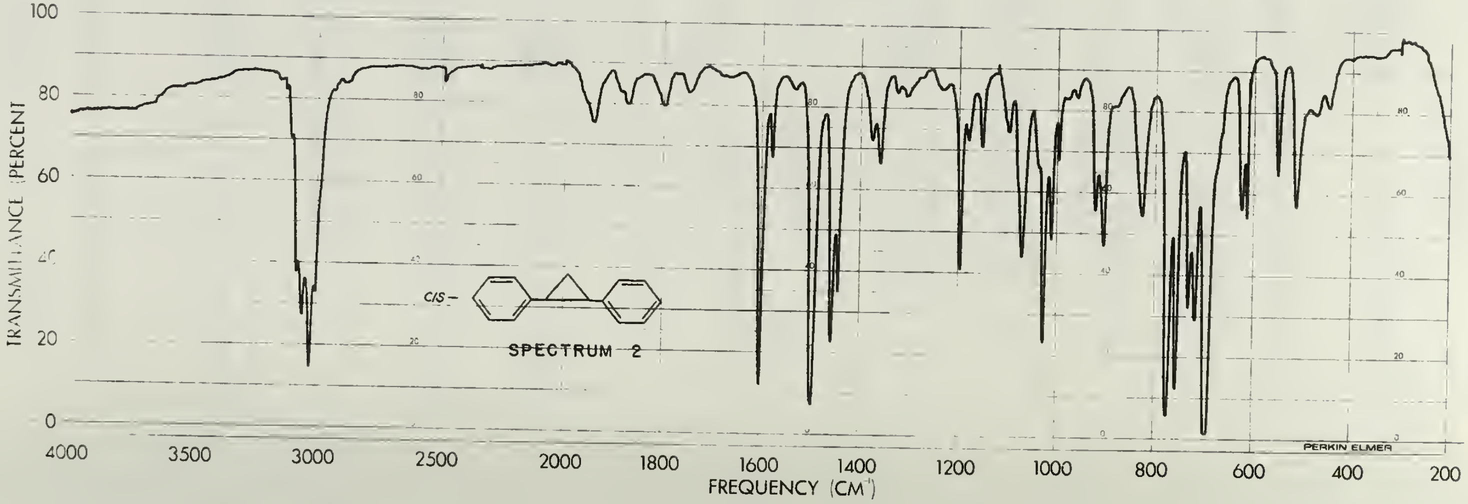

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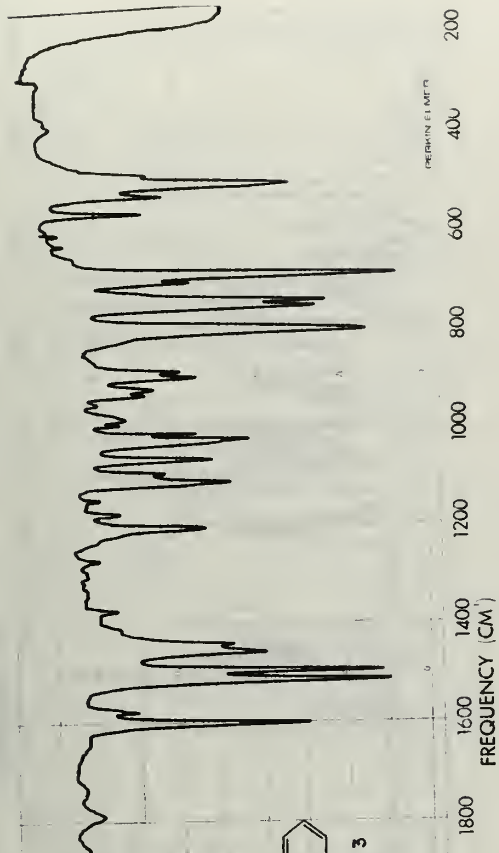

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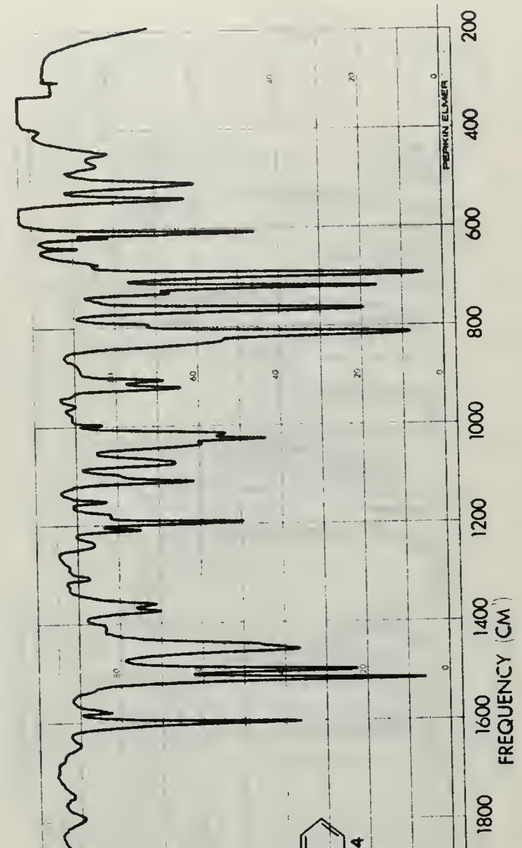

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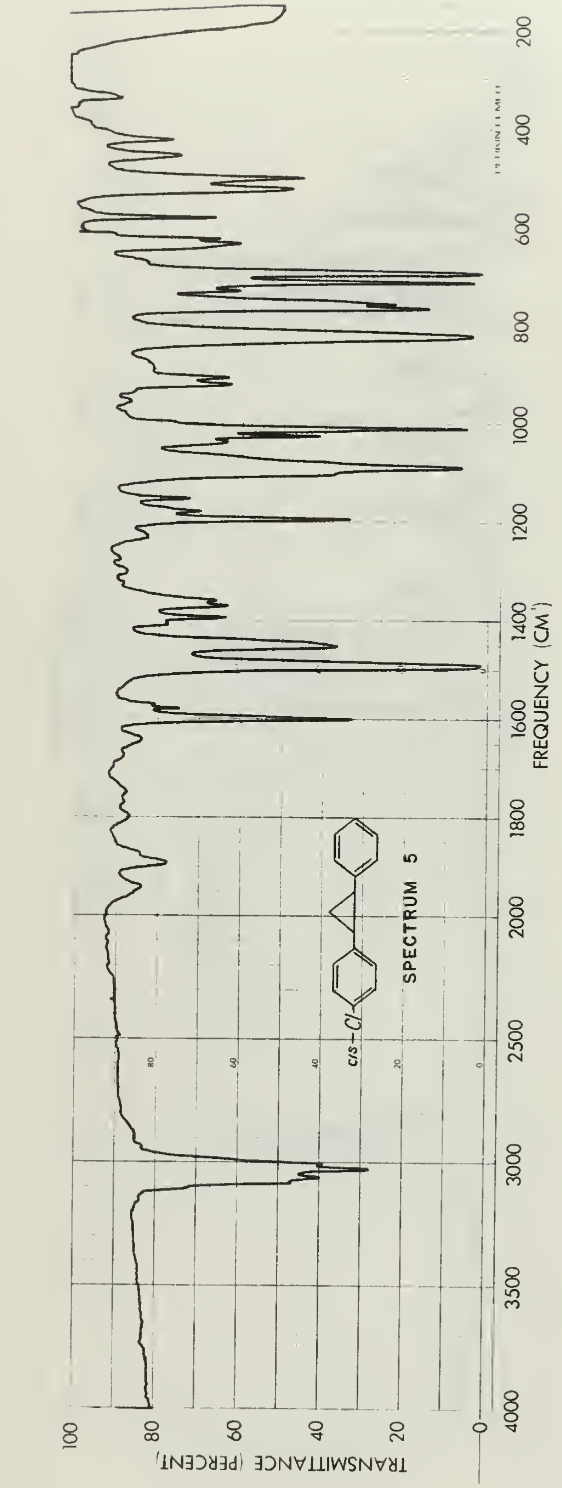

cis-Cl

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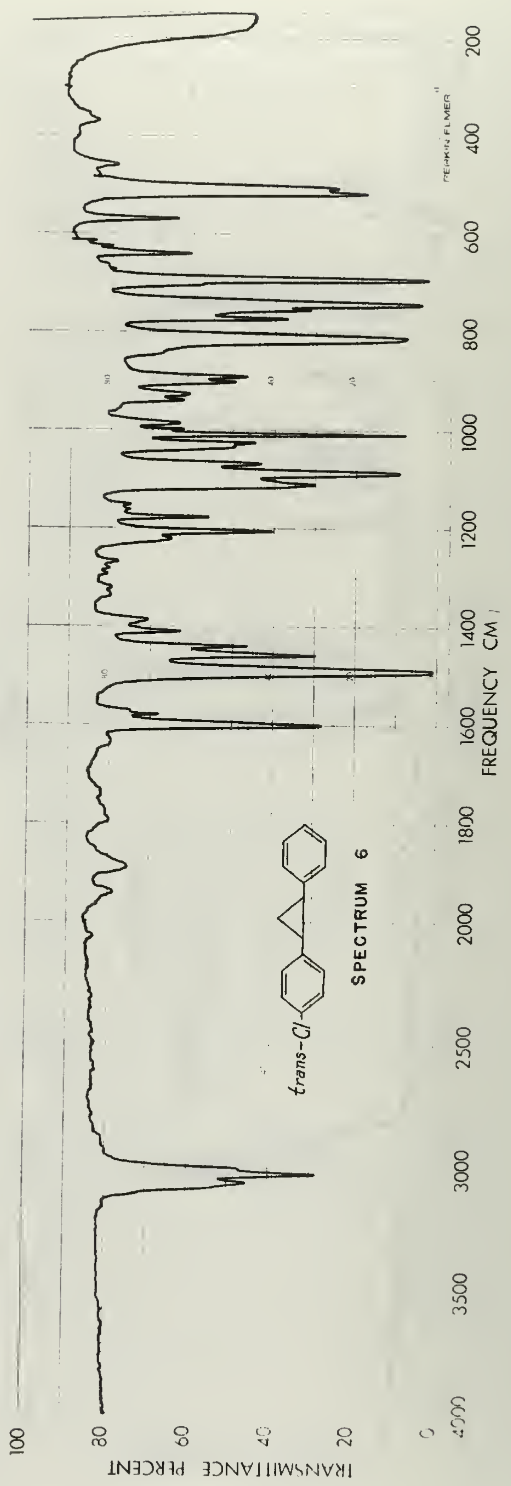

trans-Cl

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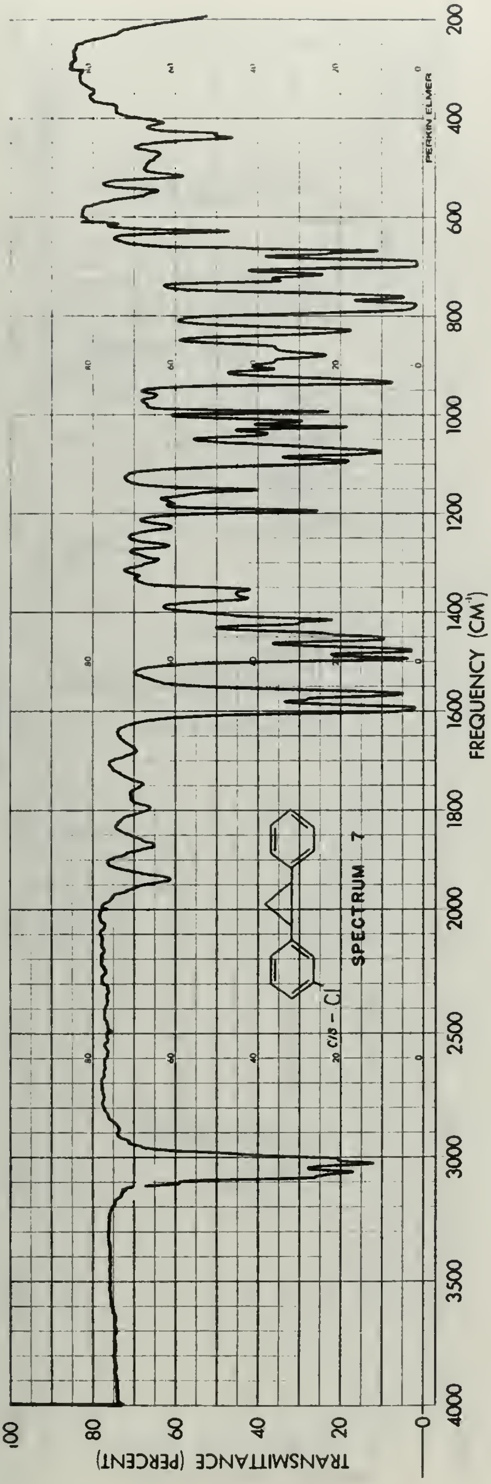

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40
20
0
FREQUENCY (CM⁻¹)
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1800
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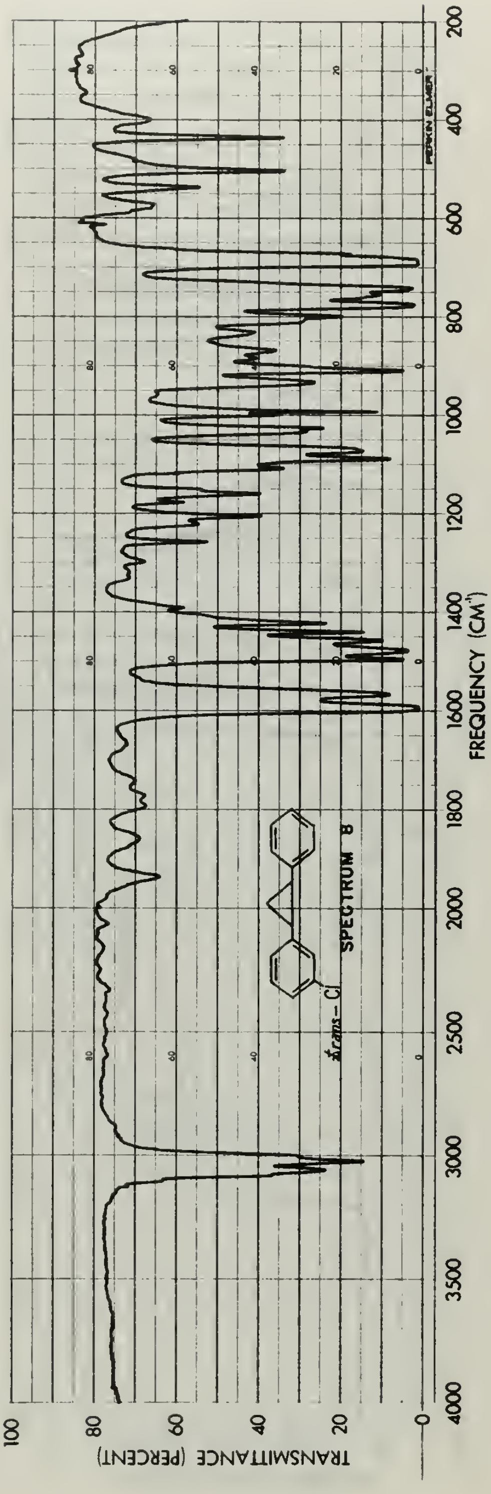
1400
1200
1000
800
600
400
200
cis – Cl
SPECTRUM 7
PERKIN ELMER



TRANSMITTANCE (PERCENT)
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20
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FREQUENCY (CM⁻¹)
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800
600
400
200
trans – Cl
SPECTRUM 8
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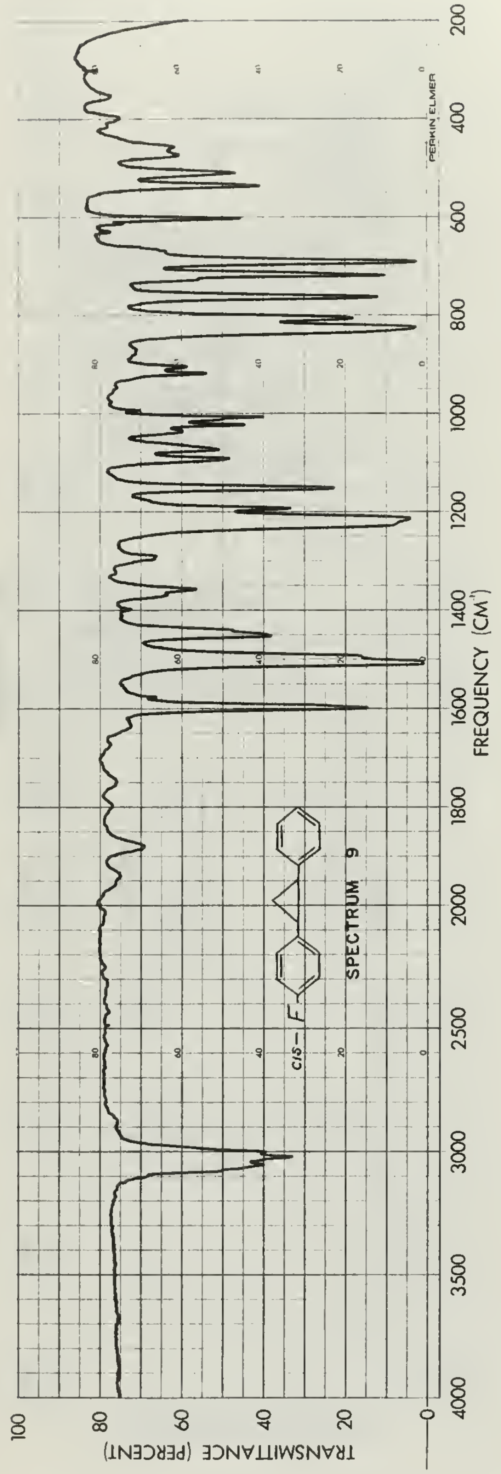

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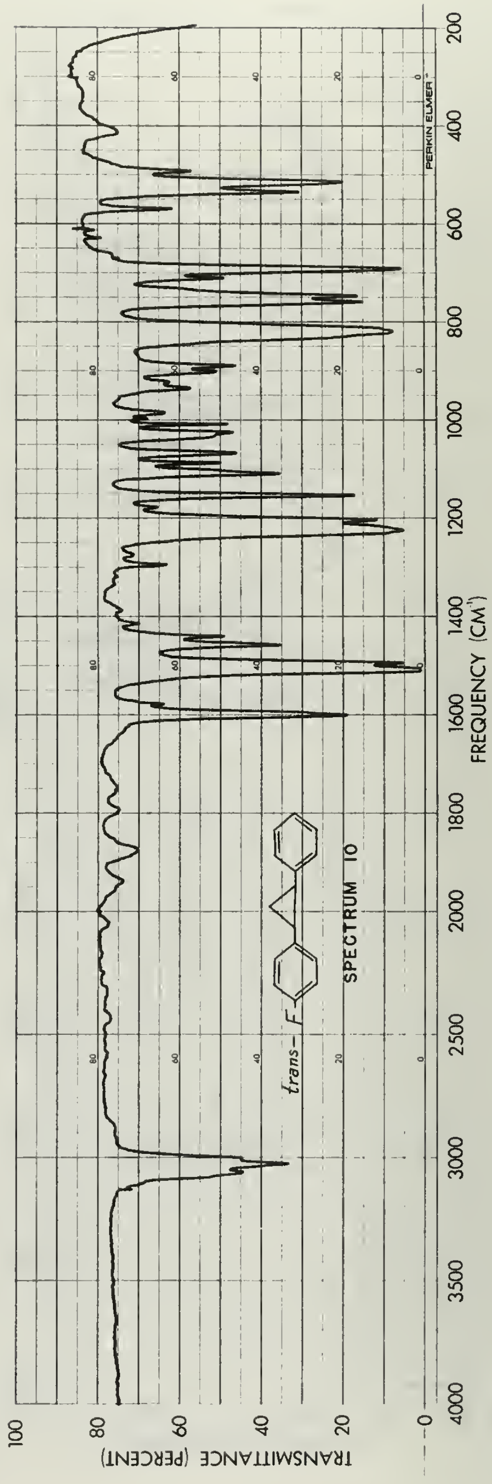

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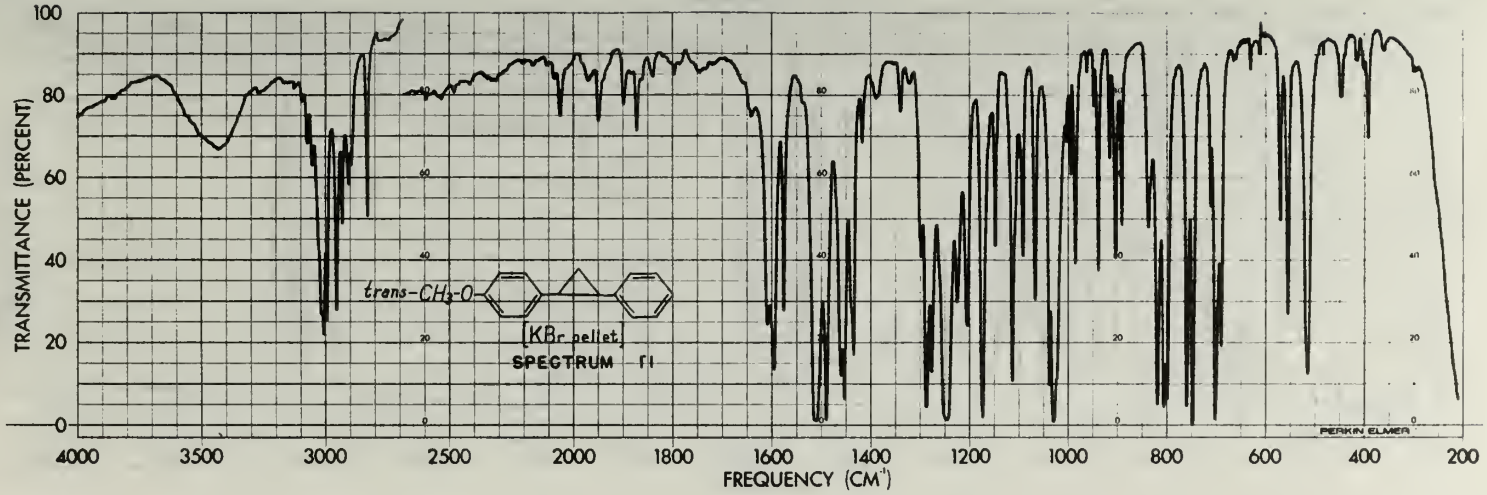

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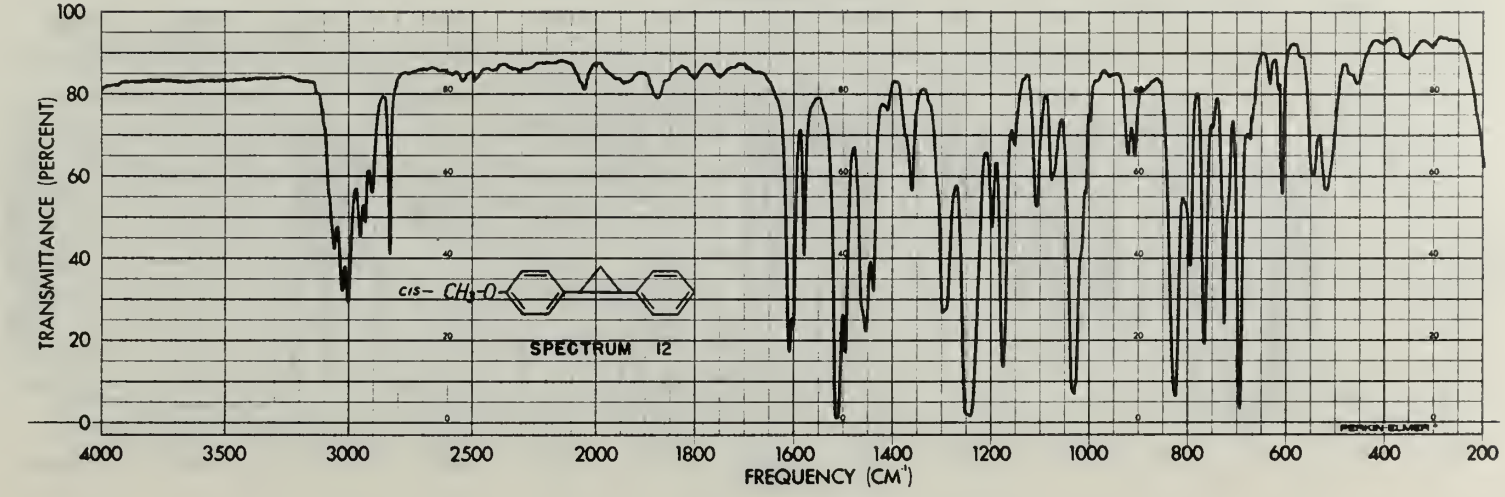

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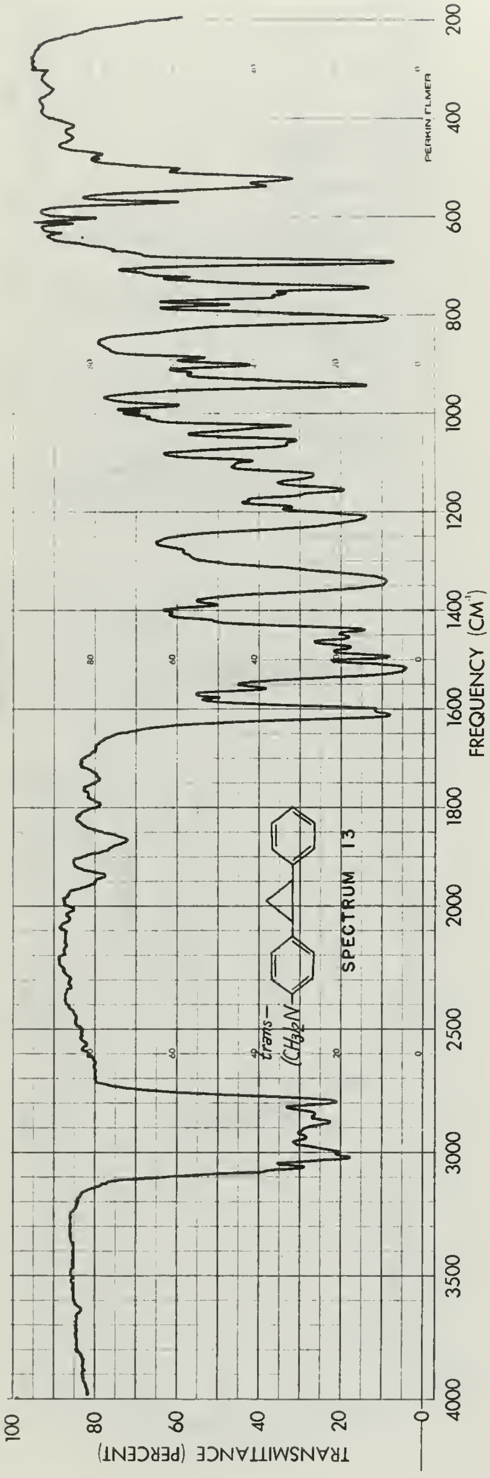

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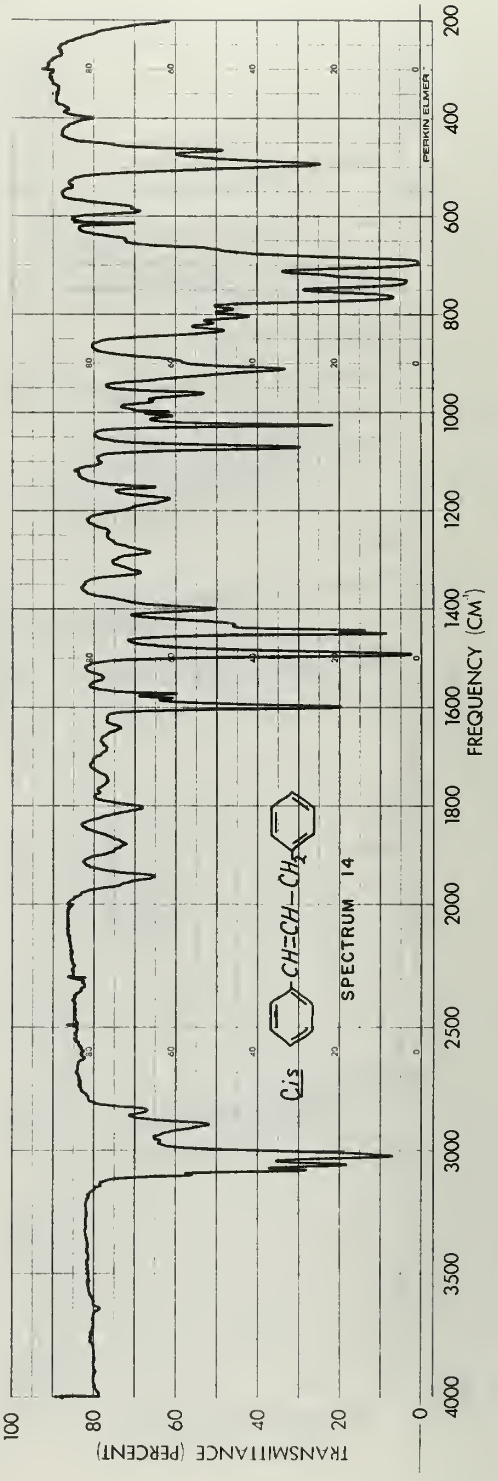

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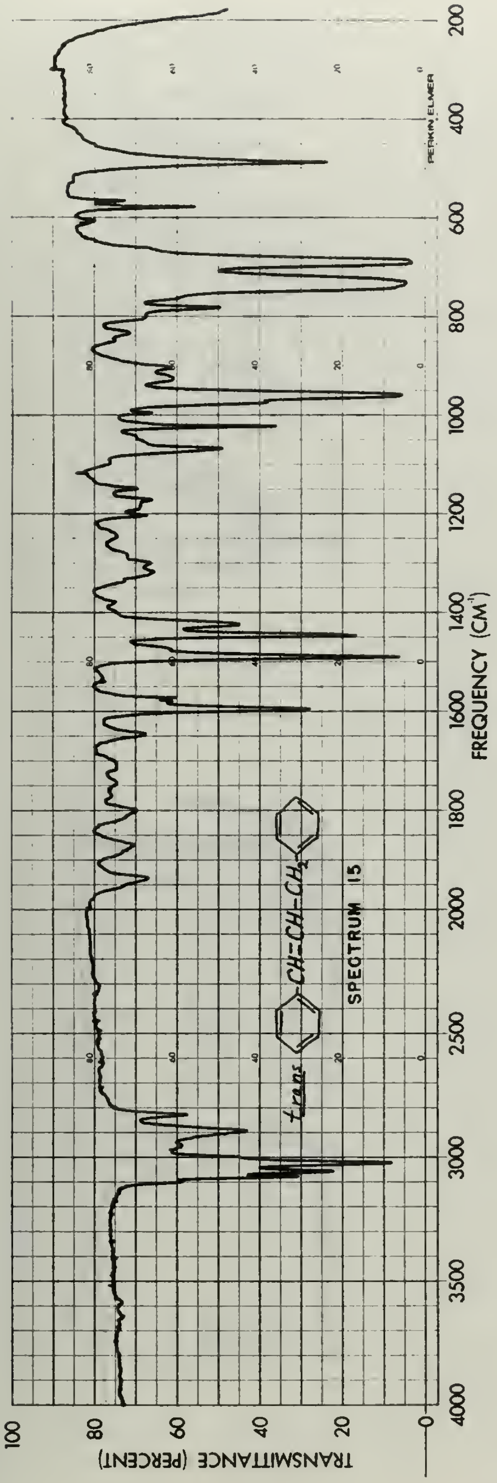

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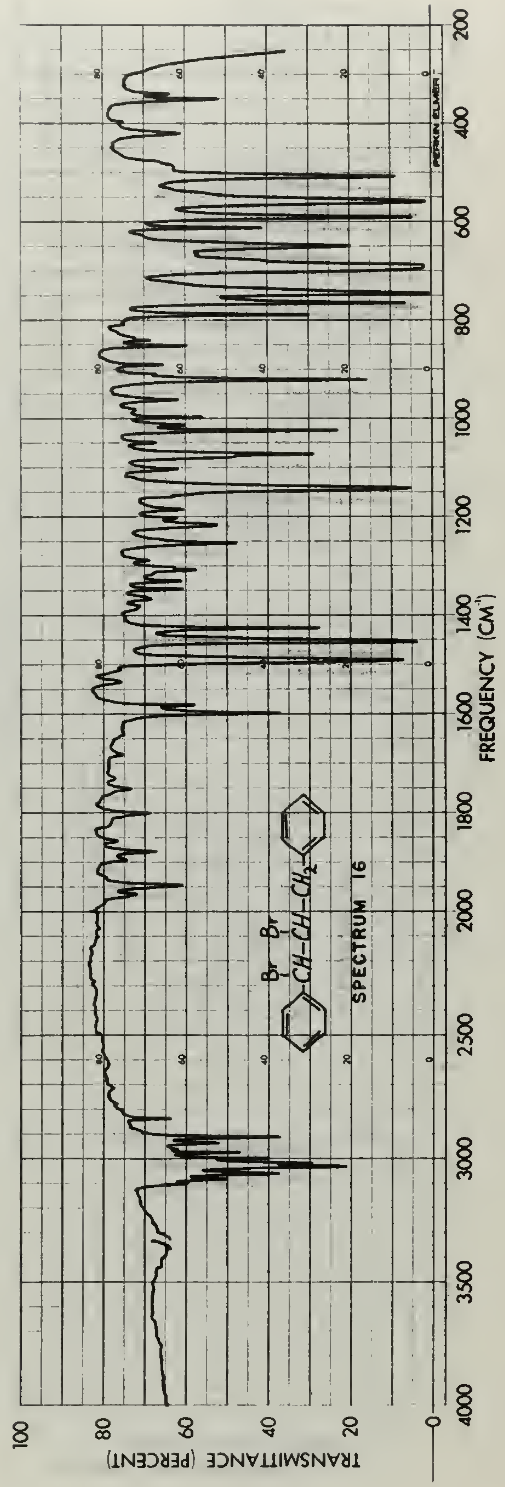

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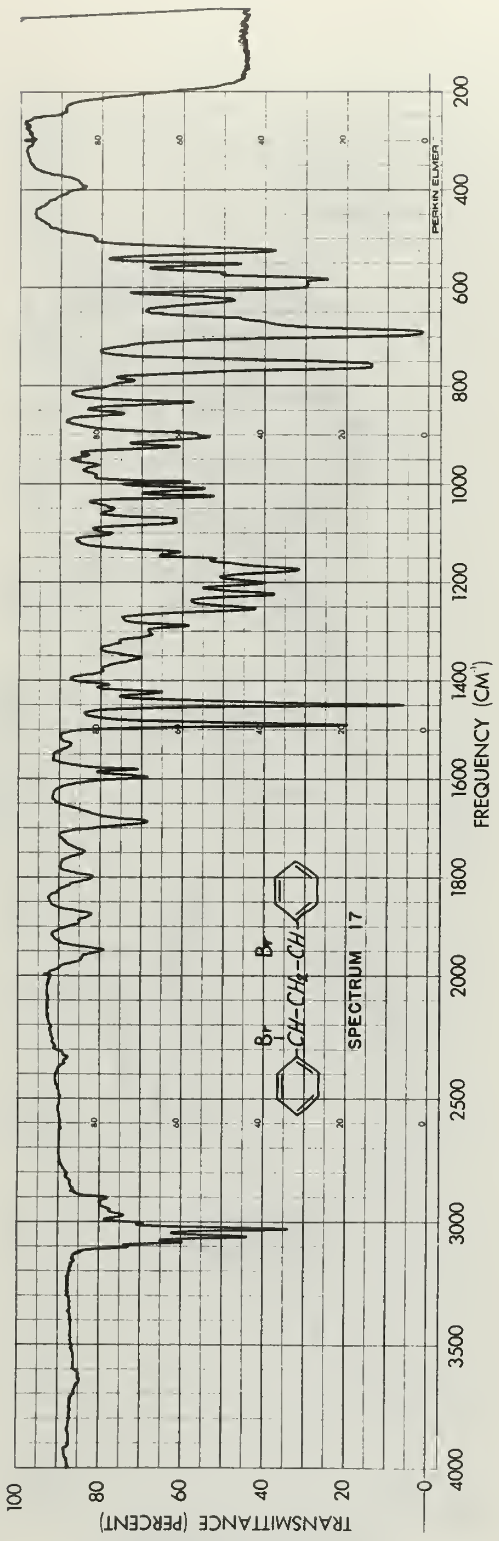

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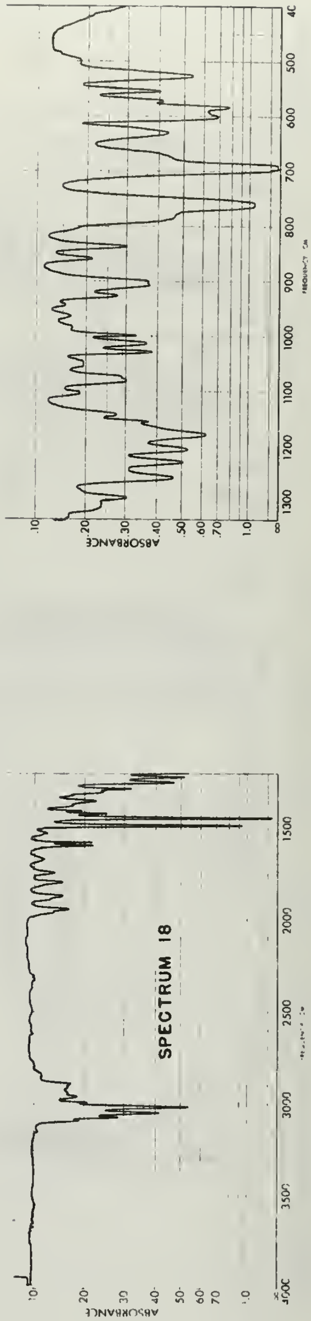

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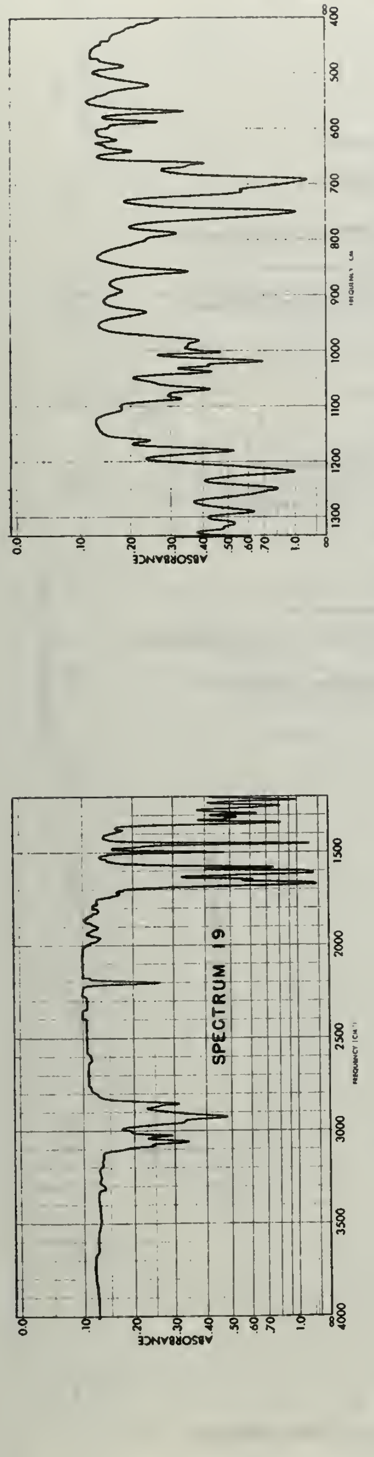

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.20
.30
.40
.50
.60
.70
1.0
∞
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3500
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2000
1500
1300
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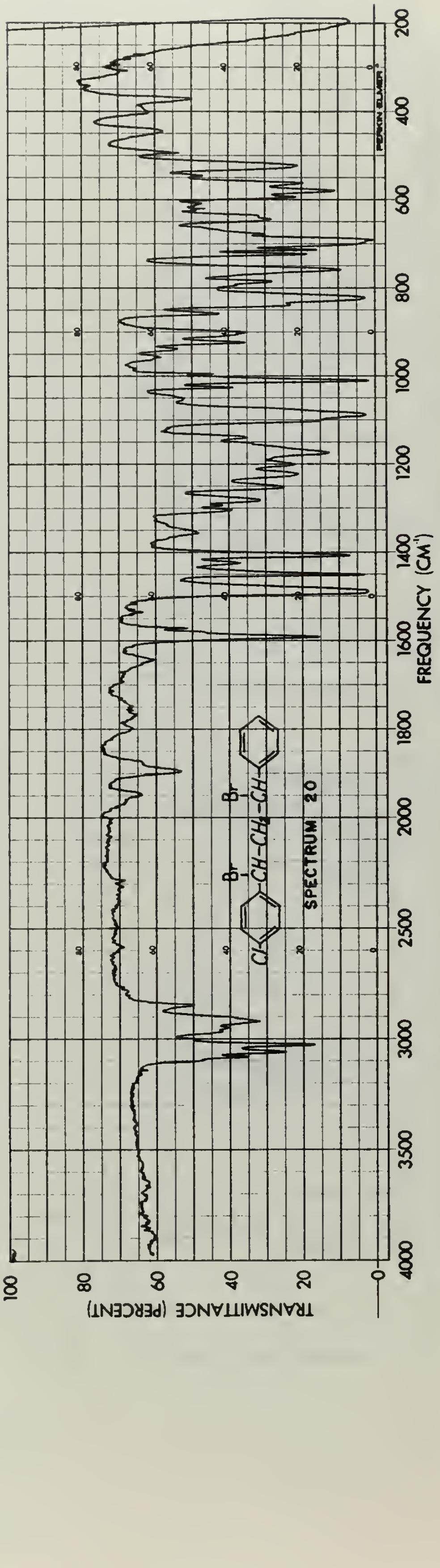
600
500
400
FREQUENCY (CM⁻¹)



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Cl-⌬-CH(Br)-CH₂-CH(Br)-⌬
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0
4000
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2000
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1600
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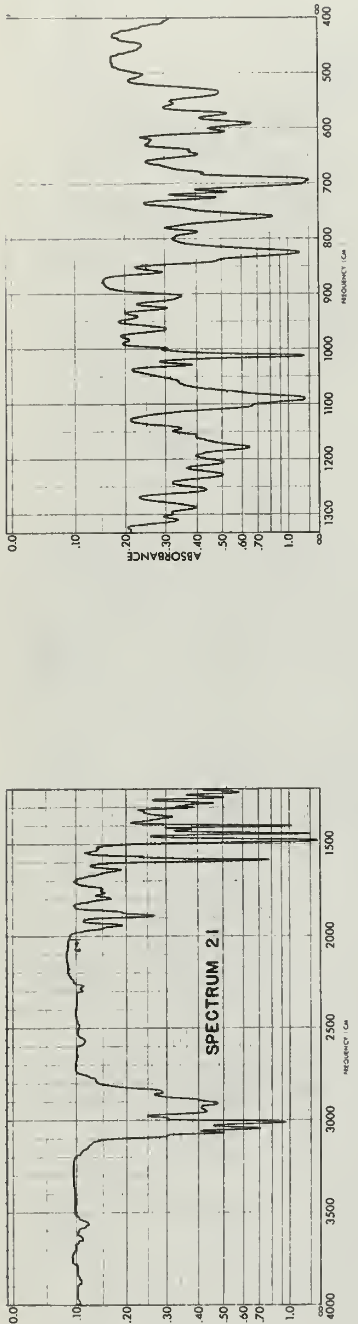
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)
PERKIN ELMER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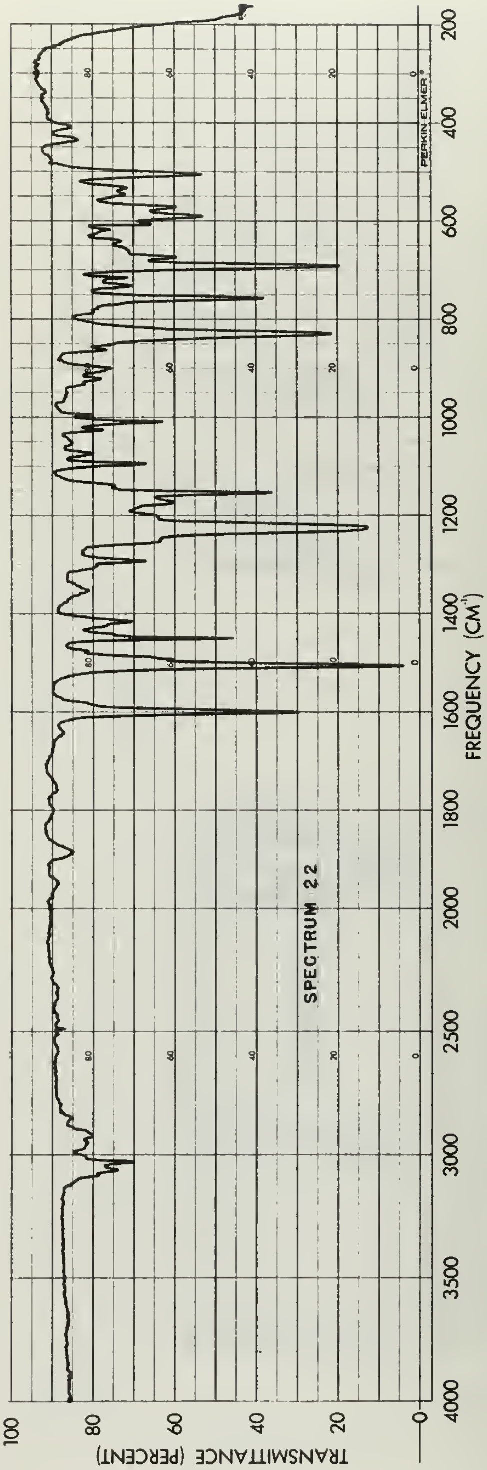
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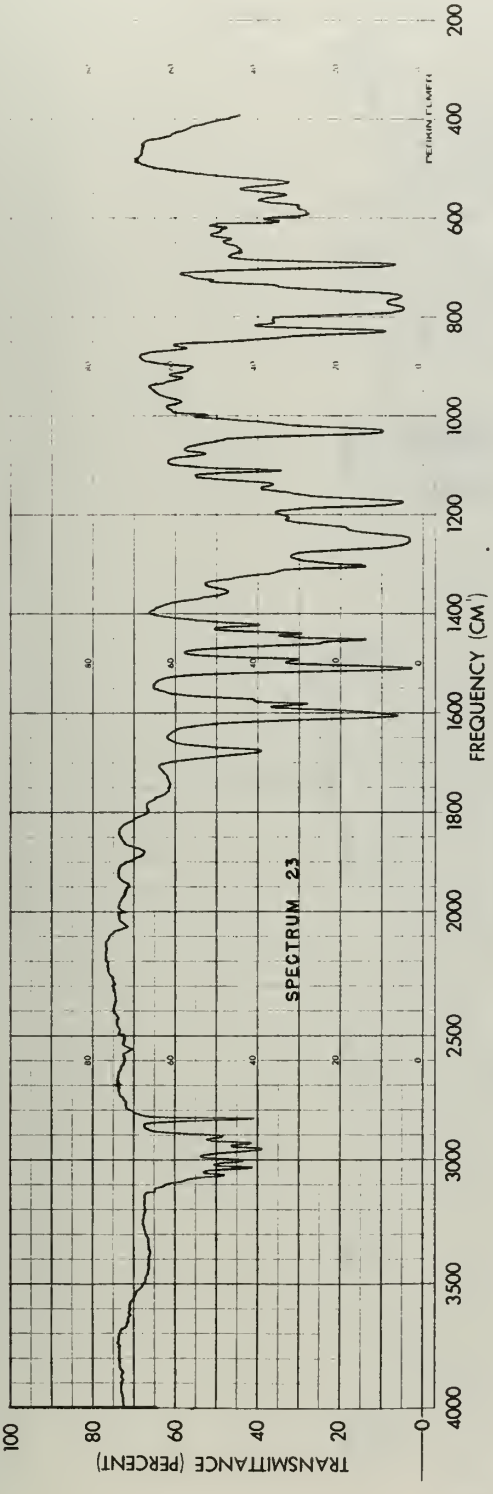
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FREQUENCY (CM⁻¹)
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800
600
400
200
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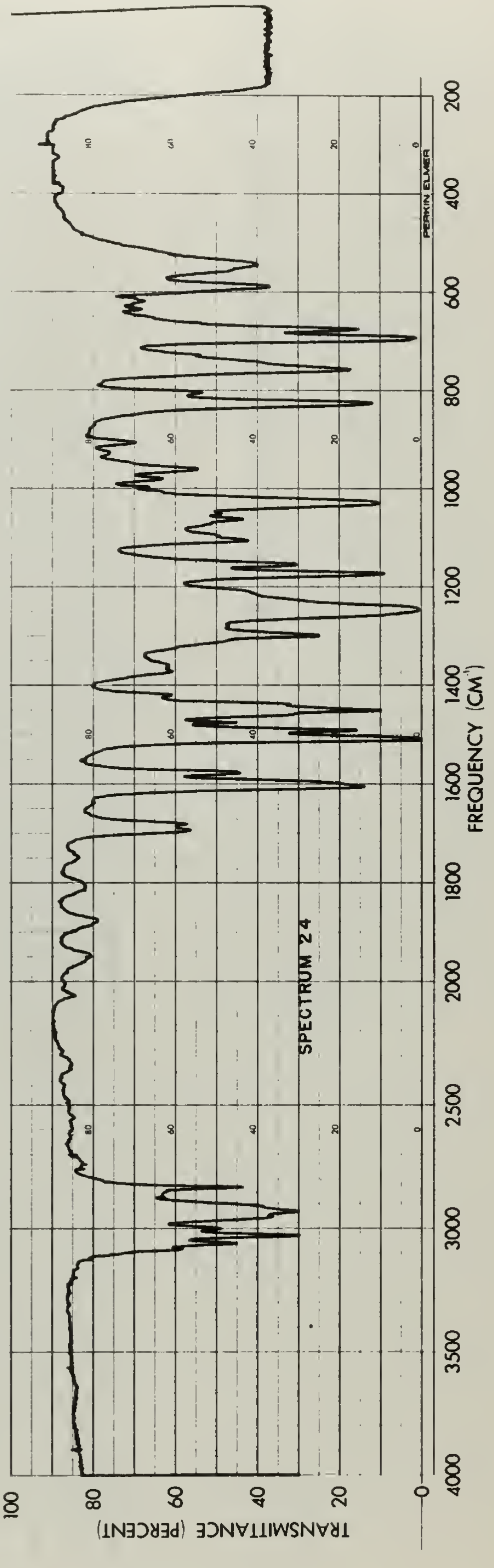
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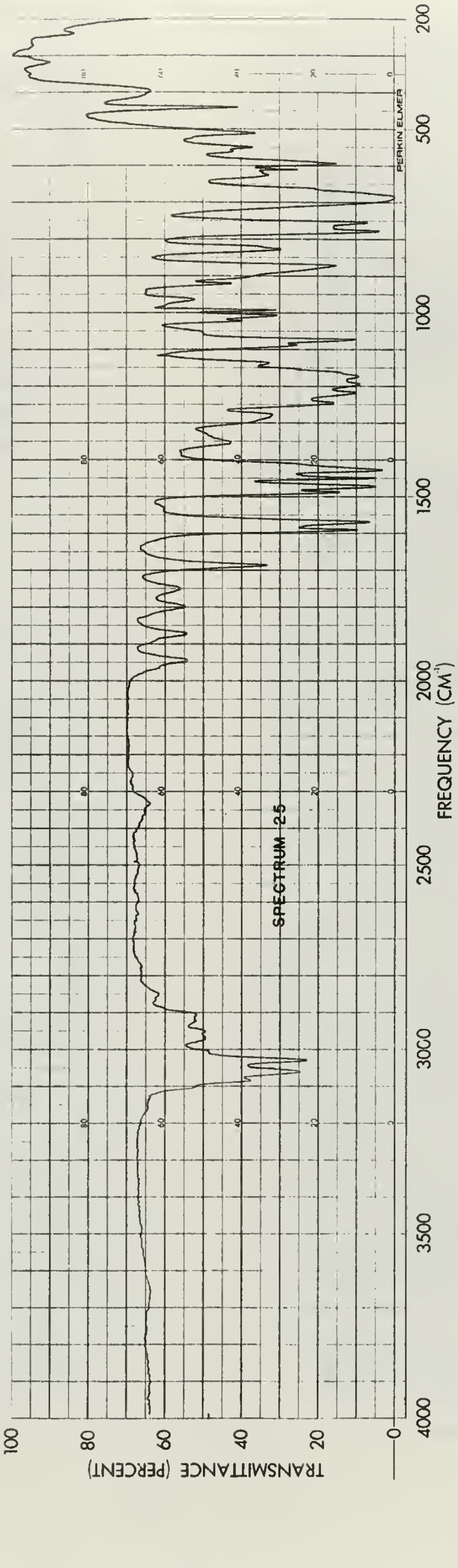
400
200
PERKIN ELMER



SPECTRUM 25

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FREQUENCY (CM⁻¹)
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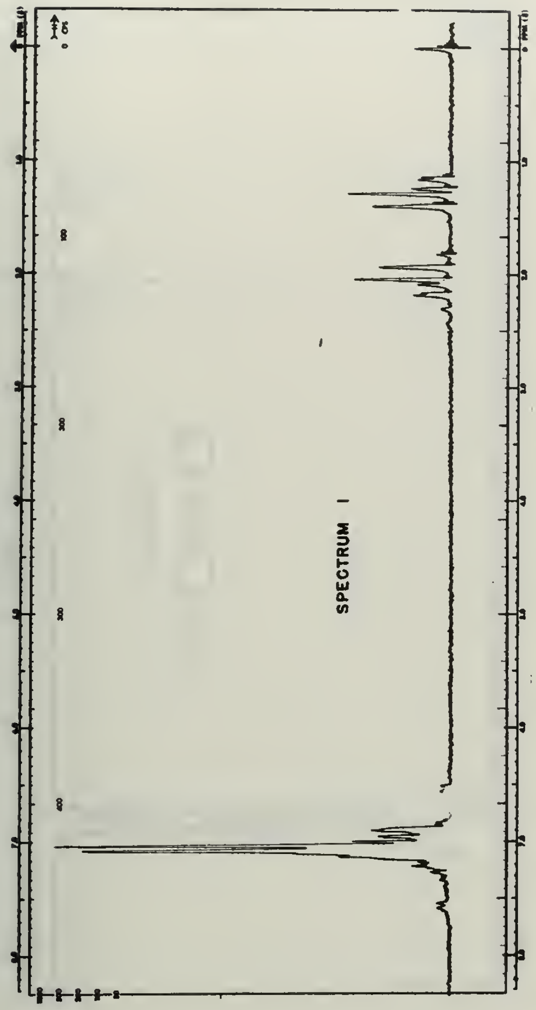
3000
2500
2000
1500
1000
500
200
PERKIN ELMER

Appendix II

APPENDIX II

The proton magnetic resonance spectra recorded in this Appendix were recorded on a Varian Model A-60 Spectrometer. The spectra were recorded at 60 MC in either carbon tetrachloride or deuterochloroform using tetramethylsilane as an internal standard. The table of contents for this Appendix appears in Appendix I.

All of the spectra were recorded at the Michelson Laboratory, Naval Ordnance Test Station, China Lake, California by Donald W. Moore. His assistance is gratefully acknowledged.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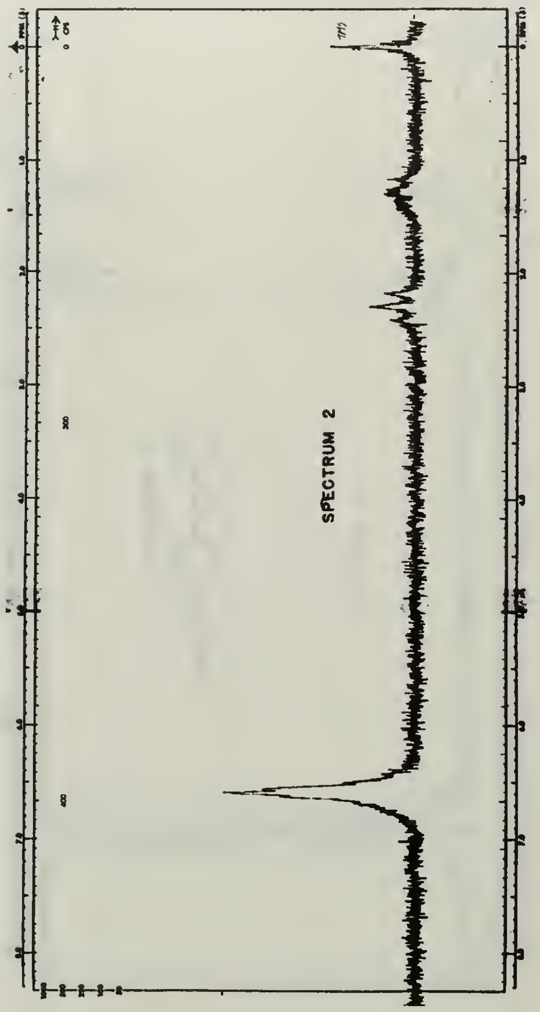
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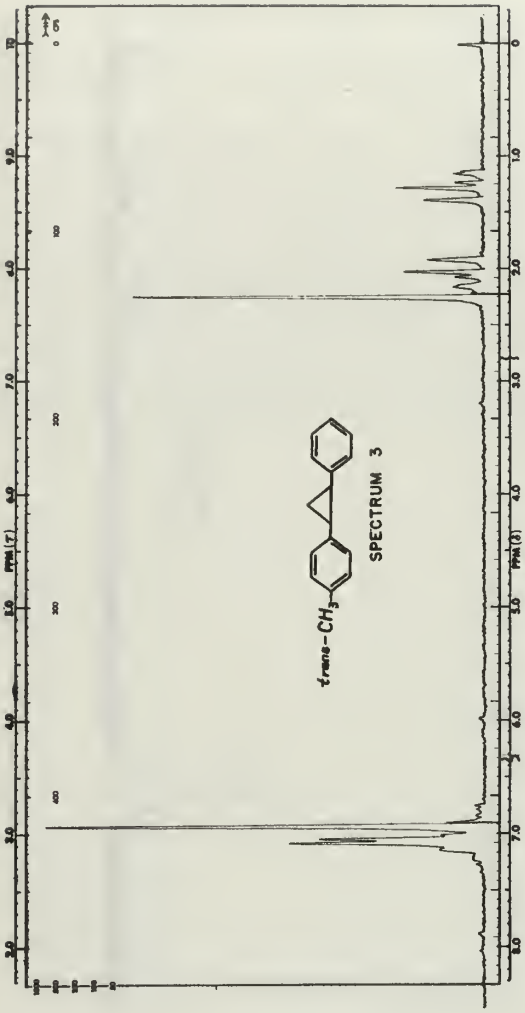

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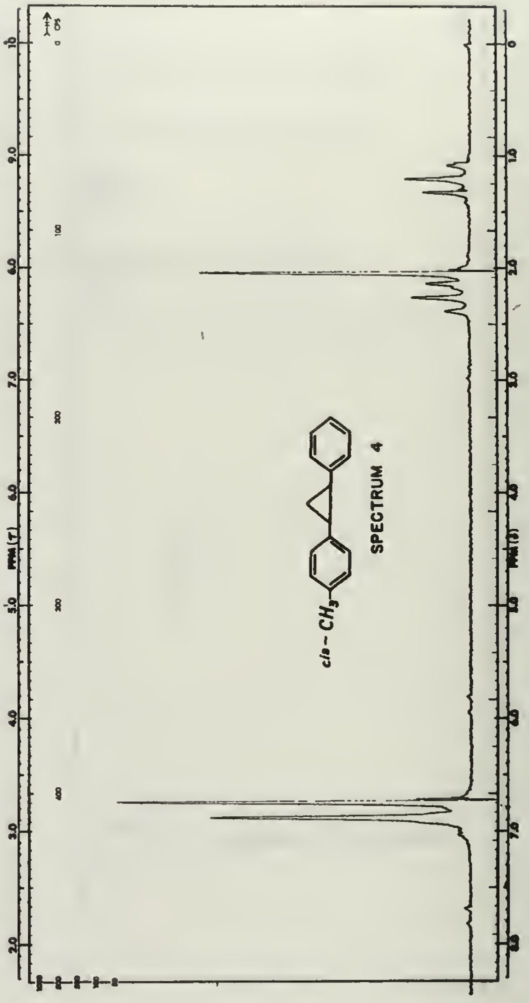

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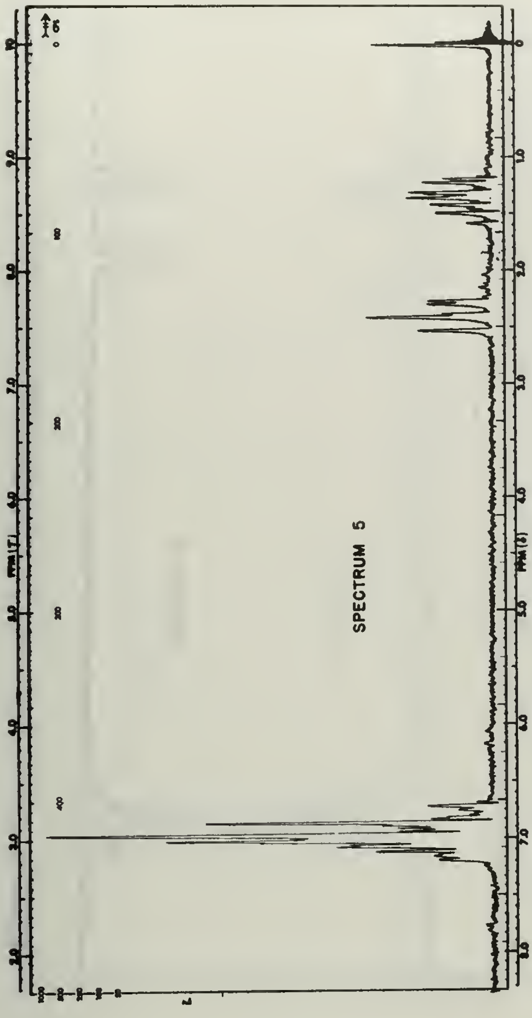

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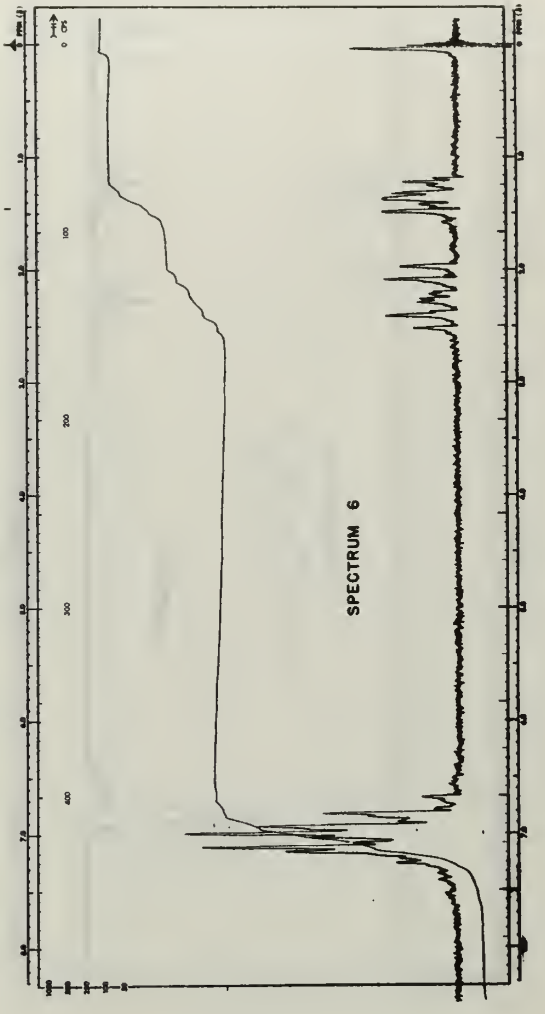

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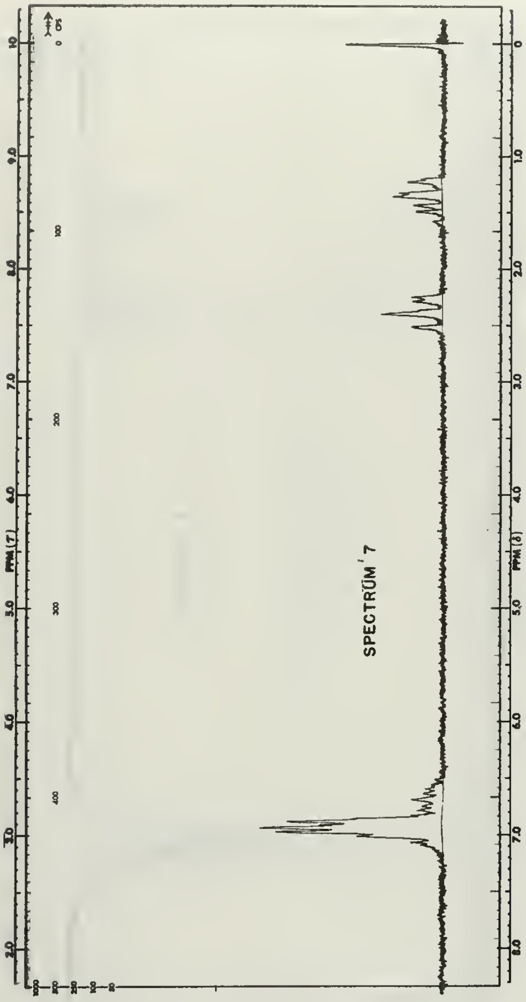

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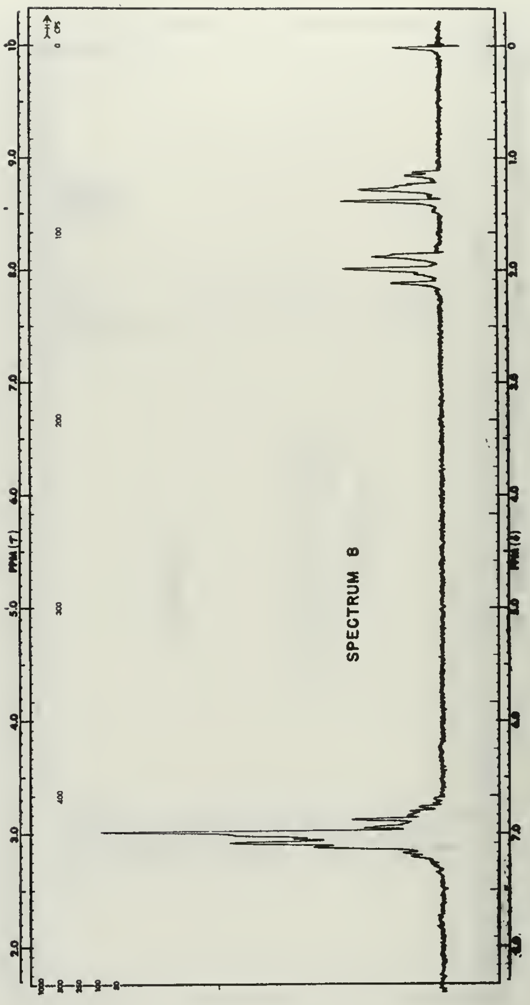

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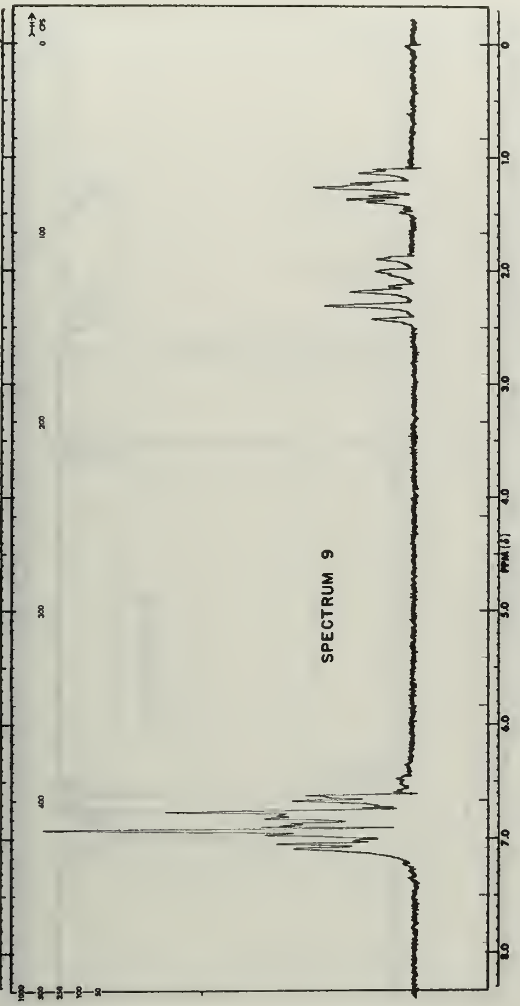

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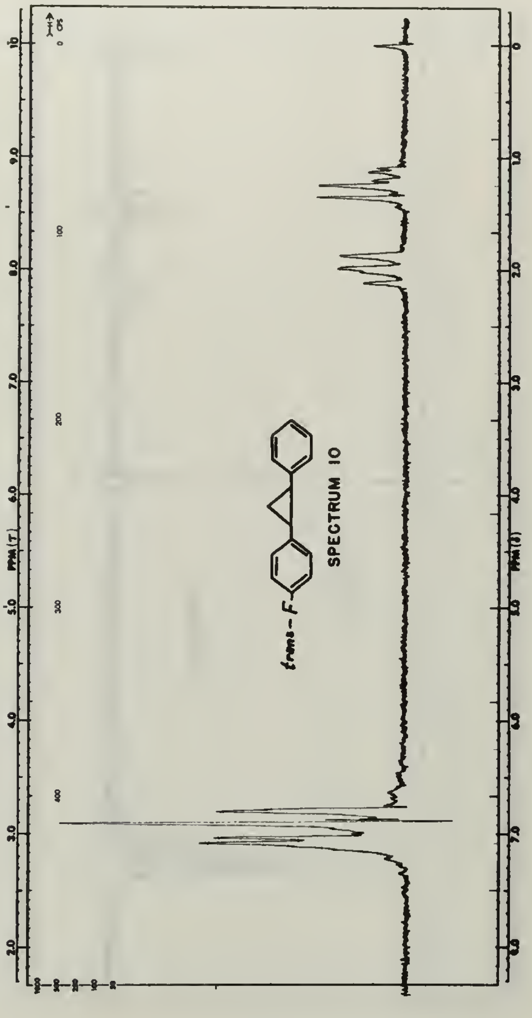
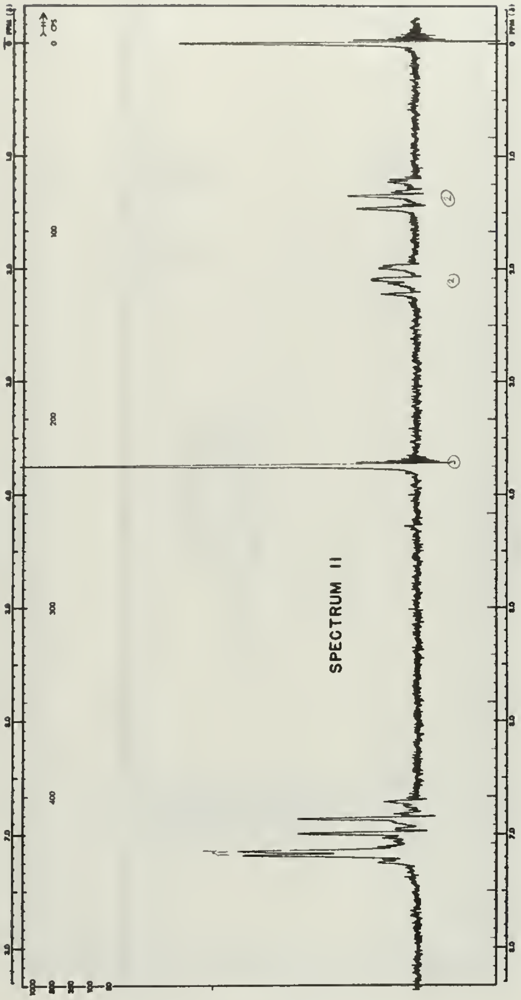


trans-F-

SPECTRUM 10



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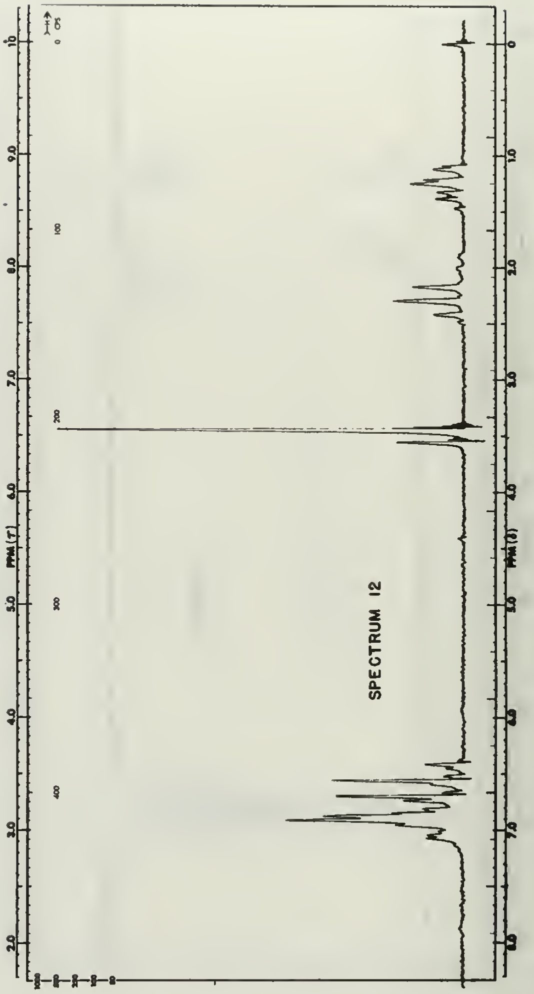

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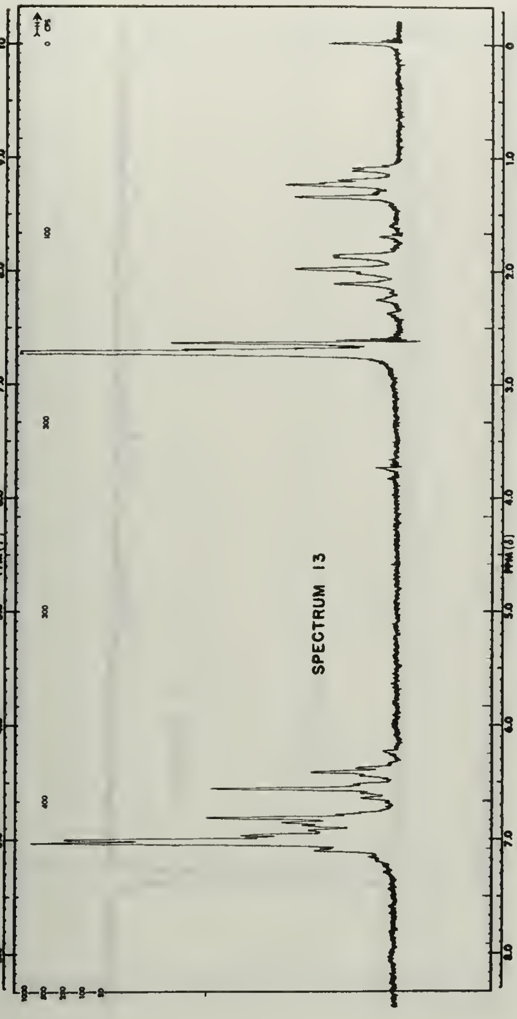

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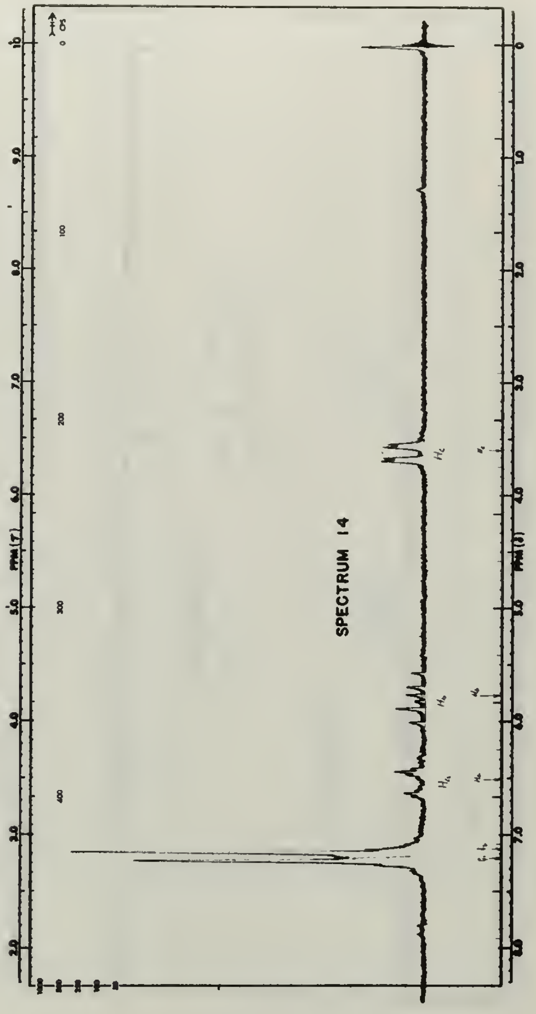

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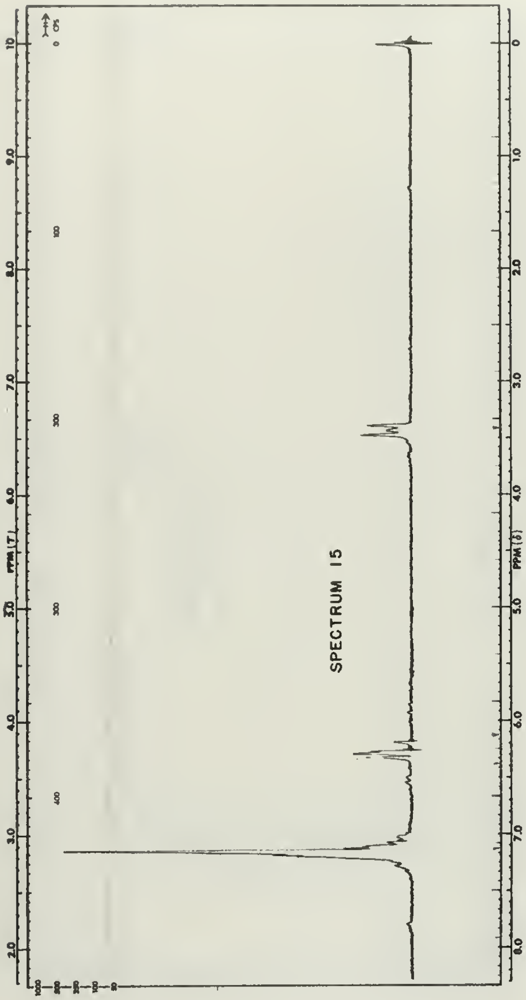
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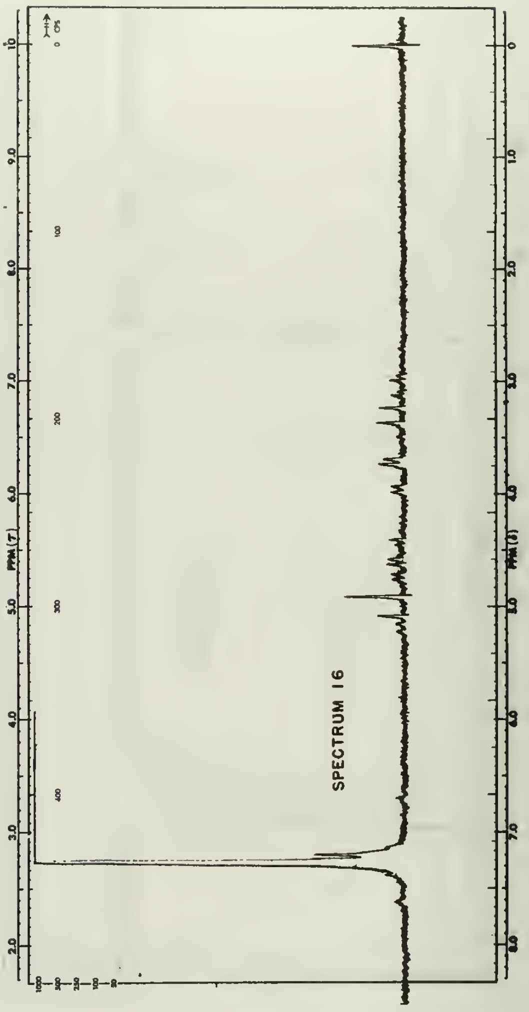
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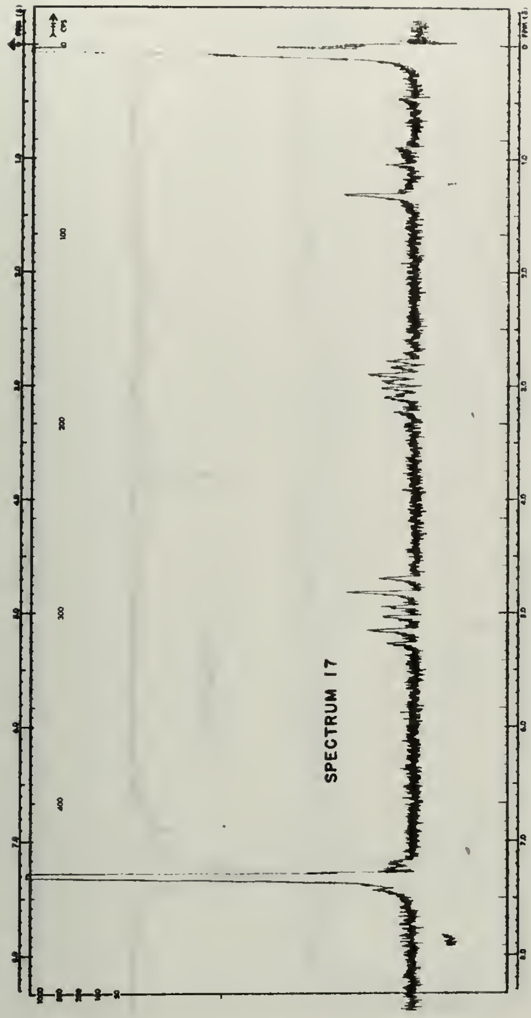

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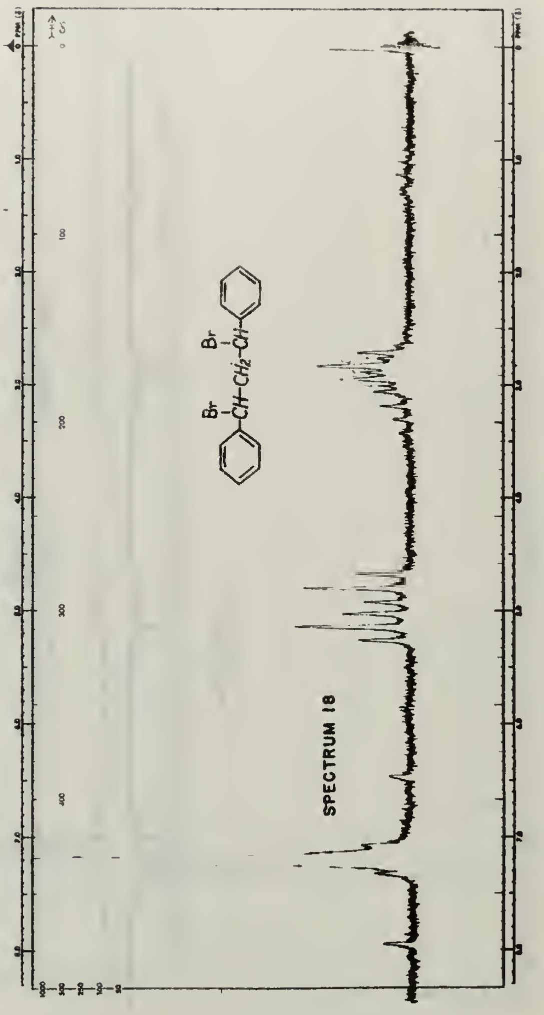

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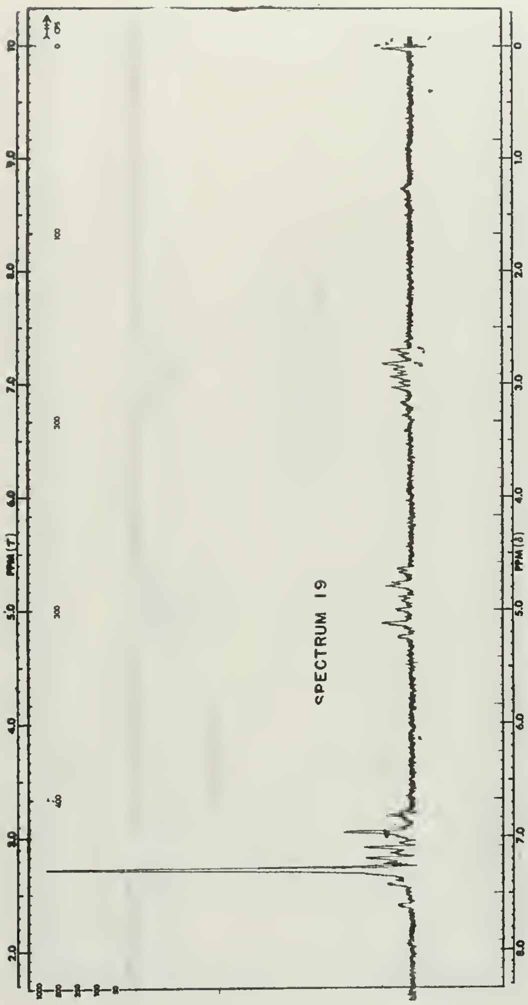

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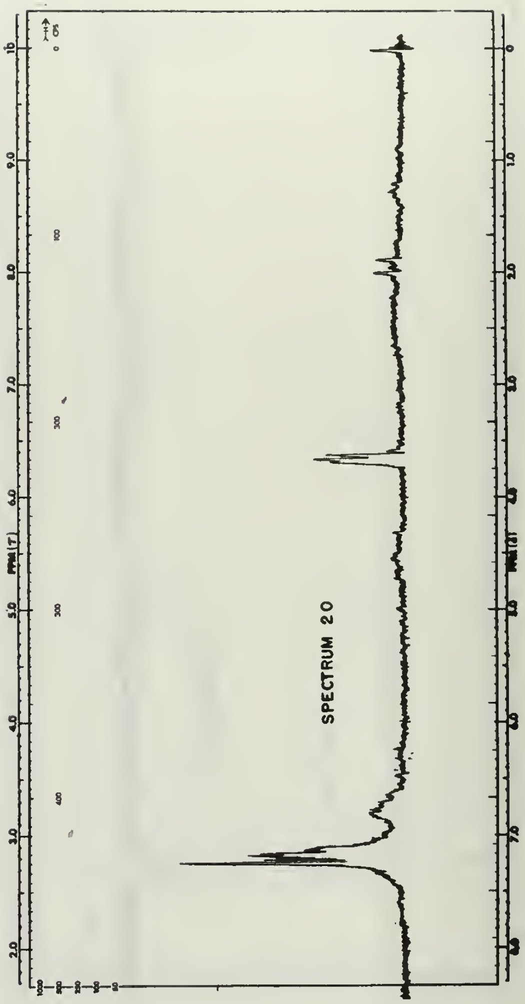

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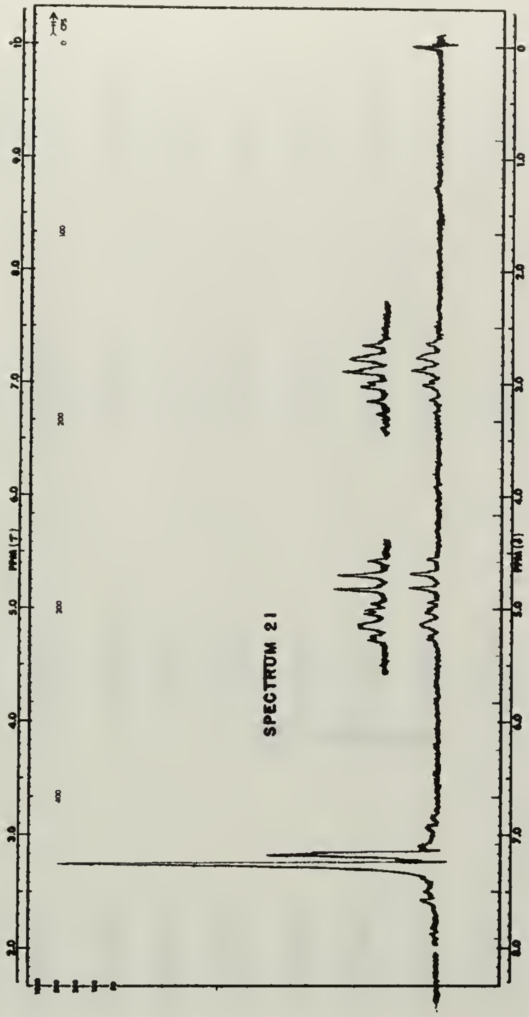
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6.0
7.0
8.0
9.0
10
400
300
200
100
0 CPS
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

SPECTRUM 21

Appendix III

Kinetic Run #9

0.10 molar in bromine

0.10 molar in trans -1, 2-diphenylcyclopropane

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$	(mμ)
0	0.540	0.735	1.36	600
2	0.460	0.679	1.47	600
4	0.390	0.624	1.60	600
6	0.325	0.570	1.75	600
8	0.272	0.522	1.92	600
10	0.230	0.480	2.08	600
12	0.198	0.445	2.25	600
14	0.164	0.405	2.47	600
16	0.753	0.869	1.15	550
18	0.640	0.800	1.25	550
20	0.544	0.739	1.35	550
24	0.400	0.632	1.58	550
28	0.310	0.557	1.79	550
32	0.270	0.522	1.92	550

Kinetic Run #10

0.053 molar in bromine

0.053 molar in _trans_ -1, 2-diphenylcyclopropane

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$	(mμ)
0	0.890	0.943	1.06	565
2	0.750	0.866	1.15	565
4	0.590	0.770	1.30	565
6	0.530	0.728	1.37	565
10	0.415	0.645	1.55	565
14	0.325	0.570	1.75	565
18	0.260	0.510	1.96	565
22	0.210	0.458	2.18	565
28	0.845	0.920	1.09	500
32	0.715	0.846	1.18	500
36	0.624	0.790	1.27	500
44	0.493	0.704	1.42	500
52	0.400	0.633	1.58	500

Kinetic Run #11

0.0512 molar in trans-1-(p-chlorophenyl)-2-phenylcyclopropane

0.0511 molar in bromine

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$	(mμ)
0	0.713	0.845	1.18	570
3	0.552	0.744	1.34	570
5	0.481	0.694	1.44	570
9	0.370	0.609	1.64	570
13	0.295	0.545	1.83	570
17	0.240	0.490	2.04	570
17	0.810	0.900	1.11	529
19	0.736	0.858	1.17	529
21	0.672	0.820	1.22	529
25	0.570	0.755	1.32	529
29	0.493	0.703	1.42	529
33	0.432	0.658	1.52	529
37	0.385	0.621	1.61	529

Kinetic Run #12

0.0460 molar in *trans*-1, 2-diphenylcyclopropane

0.0455 molar in bromine

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$	(mμ)
0	0.662	0.815	1.23	570
3	0.600	0.775	1.29	570
5	0.570	0.755	1.32	570
7	0.542	0.737	1.36	570
9	0.515	0.719	1.39	570
11	0.489	0.700	1.43	570
15	0.440	0.664	1.51	570
19	0.399	0.632	1.58	570
23	0.362	0.602	1.66	570
33	0.988	0.994	1.01	530
37	0.905	0.951	1.05	530
41	0.831	0.913	1.09	530
45	0.770	0.878	1.14	530
49	0.715	0.846	1.18	530
52	0.664	0.815	1.23	530

Slope from plot $1/\sqrt{A}$ vs. time = .0192 min^{-1}

Kinetic Run #13

0.0543 molar in *trans*-1-(p-methoxyphenyl)-2-phenylcyclopropane

0.0543 molar in bromine

Time (minutes)	%T	$\sqrt{A}$	$1/\sqrt{A}$	$(m\mu)$
18	36.0	0.665	1.48	570
20	38.0	0.648	1.55	570
22	40.2	0.629	1.59	570
24	42.5	0.611	1.64	570
26	44.8	0.591	1.69	570
30	51.0	0.541	1.85	570
34	55.0	0.510	1.96	570

Kinetic Run #14

0.0493 molar in *trans*-1-(p-methoxyphenyl)-2-phenylcyclopropane

0.054 molar in bromine

measured at 570 $m\mu$

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$
0	.796	.892	1.12
2	.744	.863	1.16
4	.694	.835	1.20
6	.651	.807	1.24
8	.601	.775	1.29
10	.556	.746	1.34
12	.501	.709	1.41
16	.387	.622	1.61

Kinetic Run #18

0.0513 molar in cis-1-(p-chlorophenyl)-2-phenylcyclopropane

0.0513 molar in bromine

measured at 570 mμ

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$
0	0.750	0.866	1.15
2	0.710	0.843	1.19
4	0.666	0.815	1.23
6	0.630	0.794	1.26
8	0.598	0.772	1.30
10	0.562	0.750	1.33
14	0.496	0.703	1.42
18	0.438	0.661	1.51
22	0.387	0.622	1.61
26	0.338	0.581	1.72
30	0.302	0.549	1.82
38	0.237	0.486	2.06
46	0.190	0.436	2.29

$1/\sqrt{A}$ vs. time - linear
Slope from curve = 0.0188 $(\text{min})^{-1}$

Kinetic Run #19

0.0492 molar in trans-1-(p-chlorophenyl)-2-phenylcyclopropane

0.0492 molar in bromine

measured at 570 mμ

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$
2	0.727	0.852	1.17
6	0.672	0.819	1.22
10	0.628	0.792	1.26
14	0.586	0.765	1.3.
18	0.548	0.740	1.35
22	0.512	0.715	1.40
26	0.480	0.692	1.45
36	0.409	0.639	1.56
46	0.353	0.594	1.68
56	0.303	0.550	1.82

$1/\sqrt{A}$ vs. time - linear

Slope from graph = 0.0113 $(\text{min})^{-1}$

Kinetic Run #20

0.0455 molar in cis-1,2-diphenylcyclopropane

0.0455 molar in bromine

measured at 570 mμ

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$
0	0.688	0.830	1.20
2	0.660	0.812	1.23
4	0.637	0.798	1.25
6	0.619	0.786	1.27
8	0.600	0.775	1.29
10	0.576	0.760	1.31
14	0.540	0.735	1.36
18	0.508	0.713	1.40
22	0.497	0.691	1.45
32	0.410	0.640	1.56
42	0.352	0.594	1.68
52	0.305	0.553	1.81

$1/\sqrt{A}$ vs. time - linear

Slope from graph = 0.0112 $(\text{min})^{-1}$

Kinetic Run #21

0.0468 molar in cis-1,2-diphenylcyclopropane

0.0468 molar in bromine

measured at 570 mμ

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$
0	0.698	0.836	1.20
2	0.654	0.809	1.24
4	0.621	0.785	1.27
6	0.593	0.770	1.30
8	0.568	0.754	1.33
10	0.540	0.735	1.36
14	0.492	0.702	1.43
18	0.446	0.668	1.50
22	0.406	0.637	1.57
26	0.367	0.606	1.65
36	0.292	0.541	1.85

$1/\sqrt{A}$ vs. time - linear

Slope from graph = 0.0169 $(\text{min})^{-1}$

Kinetic Run #22

0.0521 molar in bromine

0.0521 molar in *trans*-1,2-diphenylcyclopropane

measured at 570 mμ

Time (minutes)	A	$\sqrt{A}$	$1/\sqrt{A}$
0	0.769	0.876	1.14
2	0.716	0.846	1.18
4	0.684	0.828	1.21
6	0.653	0.809	1.24
8	0.619	0.786	1.27
10	0.592	0.770	1.30
14	0.537	0.733	1.36
18	0.490	0.700	1.47
22	0.446	0.669	1.50
34	0.342	0.585	1.71

$1/\sqrt{A}$ vs. time - linear

Slope from graph=0.0157 $(\text{min})^{-1}$

Kinetic Run #28

Time	*trans* para H		*trans* para Cl		*trans* para CH_3O	
(seconds)	A	$\sqrt{A}$	A	$\sqrt{A}$	A	$\sqrt{A}$
0	0.668	0.810	0.715	0.845	0.725	0.851
60	0.650	0.806	0.710	0.844	0.670	0.819
240	0.597	0.773	0.650	0.806	0.580	0.762
480	0.552	0.743	0.570	0.755	0.493	0.703
600	0.531	0.729	0.550	0.742	0.461	0.680
720	0.510	0.715	0.531	0.729	0.429	0.655
960	0.467	0.648	0.494	0.703	0.373	0.611
1260	0.420	0.649	0.452	0.673	0.320	0.566
1770	0.352	0.594	0.386	0.622	0.260	0.510
-slope* (X 10^3 X sec)	7.15		6.20		11.7	
Initial conc. (mmols/l)	38.5		42.3		36.0	
Initial Br2 conc. (mmols/l)	3.21		3.44		3.49	

*From plot of $\sqrt{A}$ vs. time

Absorbances measured on Beckman Model DB

Kinetic Run #29

Time	*trans* para H		*trans* para Cl		trans para CH_3O	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.560	1.34	0.560	1.34	0.570	1.33
100	0.546	1.35	0.547	1.35	0.546	1.34
200	0.535	1.38	0.538	1.38	0.535	1.38
400	0.512	1.40	0.515	1.39	0.500	1.41
800	0.466	1.47	0.473	1.46	0.446	1.50
1250	0.420	1.54	0.430	1.52	0.388	1.64
1600	0.386	1.64	0.399	1.58	0.350	1.69
2050	0.341	1.71	0.361	1.66	0.303	1.81
2500	0.292	1.85	0.315	1.78	0.260	1.96
3250	0.230	2.08	0.259	1.96	0.203	2.22
Slope* ($X 10^3$ X Sec)	4.45		4.04		5.40	
Initial conc. (mmols/1)	2.89		2.85		2.91	
Initial Br2 conc. (mmols/1)	2.69		2.69		2.69	

*From plot of $1/\sqrt{A}$ vs. time

Absorbances measured on Beckman Model DB

Kinetic Run #30

Time	*cis* para H		*cis* para Cl		*cis* para CH_3O	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.525	1.38	0.528	1.38	0.532	1.37
100	0.505	1.41	0.511	1.40	0.512	1.40
200	0.490	1.43	0.495	1.42	0.491	1.43
300	0.473	1.45	0.480	1.44	0.471	1.46
400	0.460	1.47	0.467	1.46	0.453	1.49
600	0.429	1.53	0.440	1.51	0.420	1.54
800	0.400	1.58	0.410	1.56	0.389	1.61
1000	0.374	1.64	0.385	1.61	0.360	1.67
1570	0.312	1.79	0.327	1.75	0.298	1.83
1870	0.285	1.87	0.300	1.83	0.270	1.92
Slope* ($X\ 10^{-4}$ X sec)	2.54		2.33		2.93	
Initial conc. (mmol/l)	2.62		2.56		2.76	
Initial Br2 conc. (mmols/l)	2.52		2.54		2.56	

*From plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman DB

Kinetic Run #32

Time (seconds)	Area*	log Area
0	41.2	1.614
40	27.2	1.435
80	20.6	1.314
120	14.9	1.172
160	0	---

*Dimensionless area from g.p.c. data using 1 μl samples.

Plot of log Area vs. time is linear.

Initial concentration of *trans* para H = 14.8 mmols/1.

Initial Br2 concentration 0.19 mol/1

Kinetic Run #34

Time	trans para H		trans para Cl		trans para F		trans meta Cl		trans para CH_3O	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.630	1.26	0.630	1.26	0.630	1.26	0.630	1.26	0.640	1.25
200	0.560	1.34	0.570	1.33	0.570	1.33	0.598	1.29	0.579	1.32
400	0.510	1.40	0.525	1.38	0.525	1.38	0.566	1.34	0.520	1.39
650	0.452	1.49	0.474	1.45	0.476	1.45	0.520	1.39	0.463	1.47
900	0.406	1.57	0.437	1.51	0.431	1.52	0.480	1.45	0.410	1.56
1200	0.365	1.65	0.390	1.60	0.386	1.61	0.447	1.49	0.359	1.67
1500	0.325	1.75	0.353	1.68	0.348	1.69	0.410	1.56	0.310	1.77
1900	0.285	1.87	0.311	1.80	0.309	1.80	0.378	1.63	0.268	1.93
Initial conc. (mmols/1)	3.28		3.40		3.34		3.28		3.25	
Initial Br2 conc. (mmols/1)	3.03		3.03		3.03		3.03		3.08	
Slope* (X 10^4 X Sec)	3.08		2.74		2.70		1.98		3.67	

*From plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DB

Kinetic Run #35

Time	trans meta Cl		trans para F		trans para H		trans para Cl		trans para CH_3O	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.875	1.07	0.875	1.07	0.870	1.07	0.865	1.08	0.885	1.08
100	0.855	1.08	0.855	1.08	0.850	1.09	0.852	1.08	0.848	1.09
250	0.845	1.09	0.845	1.09	0.840	1.09	0.845	1.08	0.800	1.12
550	0.805	1.11	0.798	1.10	0.792	1.13	0.805	1.11	0.720	1.18
904	0.760	1.15	0.727	1.18	0.720	1.18	0.742	1.16	0.640	1.25
1300	0.702	1.19	0.648	1.24	0.630	1.26	0.678	1.21	0.555	1.34
1850	0.635	1.25	0.555	1.34	0.540	1.36	0.592	1.30	0.450	1.49
2500	0.550	1.35	0.470	1.46	0.450	1.49	0.510	1.40	0.350	1.69
Initial conc. (mmols/l)	4.24		4.31		4.06		4.17		4.28	
Initial Br2 conc. (mmols/l)	4.21		4.21		4.18		4.15		4.27	
Slope* (X 10^4 Sec)	1.12		1.76		1.83		1.47		2.54	

*From plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DB

Kinetic Run #36

Time	trans meta Cl		trans para H		trans para Cl		trans para CH_3O		trans para F	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.642	1.25	0.640	1.25	0.640	1.25	0.655	1.24	0.640	1.25
150	0.633	1.26	0.633	1.26	0.631	1.26	0.630	1.26	0.632	1.26
300	0.620	1.27	0.620	1.27	0.622	1.27	0.607	1.28	0.623	1.27
700	0.596	1.30	0.585	1.31	0.590	1.30	0.555	1.34	0.582	1.31
950	0.580	1.31	0.560	1.34	0.566	1.33	0.528	1.38	0.560	1.34
1200	0.560	1.34	0.530	1.38	0.543	1.36	0.495	1.42	0.532	1.38
1500	0.540	1.36	0.500	1.41	0.516	1.39	0.458	1.48	0.500	1.41
2200	0.490	1.43	0.430	1.52	0.458	1.48	0.375	1.63	0.434	1.52
2700	0.458	1.48	0.390	1.60	0.419	1.55	0.323	1.76	0.395	1.59
Initial conc. (mmols/1)	3.28		3.11		3.20		3.04		3.30	
Initial Br2 conc. (mmols/1)	3.07		3.07		3.07		3.13		3.07	
Slope* ($\times 10^4$ Sec.)	1.14		1.50		1.34		2.07		1.50	

*From plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DB

Kinetic Run #37

Time	trans para CH_3O		trans para F		trans meta Cl		trans para H		trans para Cl	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.600	1.29	0.590	1.30	0.590	1.30	0.590	1.30	0.587	1.30
250	0.525	1.38	0.555	1.34	0.566	1.33	0.550	1.33	0.552	1.34
510	0.480	1.44	0.519	1.39	0.540	1.36	0.510	1.40	0.520	1.39
800	0.425	1.53	0.480	1.44	0.518	1.39	0.470	1.46	0.485	1.44
1200	0.371	1.64	0.438	1.51	0.481	1.44	0.425	1.53	0.448	1.49
1600	0.325	1.76	0.400	1.58	0.450	1.49	0.386	1.61	0.412	1.56
2000	0.288	1.87	0.365	1.66	0.418	1.55	0.350	1.69	0.380	1.62
2700	0.230	2.09	0.315	1.78	0.368	1.65	0.300	1.82	0.328	1.74
3250	0.195	2.26	0.280	1.89	0.330	1.74	0.268	1.93	0.292	1.85
Initial conc. (mmols/1)	2.93		3.02		3.19		3.12		3.19	
Initial Br_2 conc. (mmols/1)	2.88		2.84		2.84		2.84		2.84	
Slope* (X 10^4 Sec)	2.98		1.76		1.27		1.85		1.63	

*From a plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DB

Kinetic Run #38

Time	*cis* para H		*cis* para Cl		*cis* meta Cl		*cis* para CH_3O	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.660	1.23	0.650	1.24	0.660	1.23	0.662	1.23
202	0.608	1.28	0.611	1.28	0.618	1.27		
905	0.473	1.45	0.502	1.41	0.510	1.40	0.470	1.46
1900	0.353	1.68	0.385	1.61	0.407	1.57	0.337	1.72
3900	0.222	2.12	0.250	2.00	0.272	1.92	0.176	2.38
Initial conc. (mmols/l)	3.36		3.23		3.17		3.52	
Initial Br_2 conc. (mmols/l)	3.17		3.12		3.17		3.18	
Slope* ($\times 10^4$ Sec.)	2.38		1.97		1.73		2.75	

*From a plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DU

Kinetic Run #39

Time (seconds)	*cis* para H A	 $1/\sqrt{A}$	*cis* para Cl A	 $1/\sqrt{A}$	*cis* meta Cl A	 $1/\sqrt{A}$	*cis* para CH_3O A	 $1/\sqrt{A}$
0	0.654	1.24	0.656	1.24	0.660	1.23	0.662	1.23
350	0.579	1.31	0.583	1.31	0.587	1.30	0.550	1.35
1117	0.427	1.53	0.451	1.49	0.470	1.46	0.371	1.64
1928	0.326	1.75	0.354	1.68	0.381	1.62	0.265	1.94
2867	0.253	1.99	0.276	1.90	0.305	7.81	0.202	2.22
Initial conc. (mmols/1)	3.05		3.26		3.42		2.68	
Initial Br2 conc. (mmols/1)	3.14		3.15		3.17		3.18	
Slope* (X 10^4 Sec.)	2.70		2.30		2.00		3.48	

*From a plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DU

Kinetic Run #40

Time	cis meta Cl		cis para H		cis para CH_3O		cis para Cl	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.860	1.08	0.861	1.08	0.870	1.07	0.870	1.07
200	0.789	1.12	0.777	1.13	0.760	1.15	0.793	1.12
605	0.660	1.23	0.633	1.26	0.612	1.28	0.660	1.23
952	0.586	1.31	0.542	1.36	0.487	1.43	0.574	1.32
1200	0.532	1.37	0.487	1.47	0.420	1.54	0.520	1.39
1655	0.458	1.48	0.407	1.57	0.332	1.73	0.442	1.50
2600	0.360	1.67	0.310	1.80	0.232	2.08	0.335	1.73
Initial conc. (mmols/1)	3.86		3.93		3.82		3.91	
Initial Br2 conc. (mmols/1)	4.18		4.18		4.18		4.18	
Slope* (X 10^4 Sec.)	2.40		2.95		3.97		2.65	

*From a plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DU

Kinetic Run #41

Time	*cis* para H		*cis* para CH_3O		*cis* meta Cl		*cis* para Cl	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.664	1.23	0.664	1.23	0.670	1.23	0.670	1.23
204	0.642	1.25	0.630	1.26	0.657	1.24	0.655	1.24
461	0.628	1.26	0.588	1.30	0.640	1.25	0.637	1.25
750	0.608	1.28	0.543	1.36	0.620	1.27	0.618	1.27
1200	0.572	1.32	0.480	1.44	0.590	1.30	0.586	1.31
1800	0.520	1.39	0.408	1.56	0.548	1.35	0.540	1.36
2450	0.463	1.47	0.338	1.72	0.500	1.41	0.491	1.43
Initial conc. (mmols/1)	3.38		3.41		3.37		3.37	
Initial Br2 conc. (mmls/1)	3.19		3.19		3.22		3.22	
Slope* (X 10^4 Sec.)	0.92		1.66		0.63		0.72	

*From a plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DU

Kinetic Run #43

Time	cis para Cl		cis meta Cl		cis para H		cis para CH_3O	
(seconds)	A	$\sqrt{A}$	A	$\sqrt{A}$	A	$\sqrt{A}$	A	$\sqrt{A}$
0	0.535	0.731	0.540	0.735	0.547	0.740	0.569	0.754
101	0.523	0.725	0.530	0.728	0.530	0.728	0.540	0.735
200	0.517	0.719	0.521	0.722	0.521	0.722	0.523	0.725
300	0.509	0.713	0.515	0.719	0.512	0.716	0.510	0.713
455	0.496	0.705	0.501	0.708	0.493	0.702	0.482	0.695
600	0.484	0.695	0.490	0.700	0.478	0.691	0.460	0.679
800	0.469	0.685	0.475	0.690	0.461	0.680	0.436	0.661
1100	0.448	0.670	0.458	0.676	0.438	0.662	0.395	0.629
1500	0.420	0.648	0.432	0.657	0.406	0.637	0.351	0.593
Initial conc. (mmols/l)	35.4		34.6		36.7		29.4	
Initial Br2 conc. (mmols/l)	2.57		2.59		2.62		2.73	
Slope* (X 10^5 Sec.)	5.5		5.4		6.8		9.8	
Slope/conc.	1.55		1.56		1.85		3.3	

*From a plot of $\sqrt{A}$ vs. time
Absorbances measured on Beckman Model DU

Kinetic Run #44

Time	trans para H		cis para F		cis para CH_3O		cis para Cl		cis meta Cl		cis para H	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.670	1.22	0.670	1.22	0.678	1.21	0.677	1.21	0.677	1.21	0.680	1.21
200	0.606	1.28	0.620	1.27	0.609	1.28	0.630	1.26	0.631	1.26	0.630	1.26
400	0.550	1.35	0.578	1.31	0.556	1.34	0.585	1.31	0.592	1.30	0.585	1.31
600	0.500	1.41	0.538	1.36	0.509	1.40	0.545	1.35	0.555	1.34	0.539	1.36
850	0.449	1.49	0.493	1.42	0.456	1.48	0.500	1.41	0.511	1.40	0.492	1.42
1100	0.405	1.57	0.457	1.48	0.408	1.57	0.462	1.47	0.475	1.45	0.450	1.49
1815	0.317	1.78	0.373	1.64	0.298	1.80	0.377	1.63	0.395	1.59	0.365	1.65
Initial conc. (mmols/l)	3.27		3.25		3.42		3.54		3.09		3.22	
Initial Br2 conc. (mmols/l)	3.22		3.22		3.26		3.26		3.26		3.27	
Slope* (X 10^4 Sec.)	3.20		2.35		3.30		2.30		2.10		2.60	

*From plot of $1/\sqrt{A}$ vs. time

Absorbances measured on Beckman Model DU

Kinetic Run #45

Time	cis para CH_3O		trans para H		cis meta Cl		cis para H		cis para F		cis para Cl	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.660	1.23	0.660	1.23	0.660	1.23	0.668	1.22	0.662	1.23	0.670	1.22
350	0.540	1.36	0.610	1.28	0.621	1.27	0.620	1.27	0.625	1.26	0.628	1.26
850	0.408	1.57	0.494	1.42	0.555	1.34	0.520	1.39	0.531	1.37	0.544	1.35
1200	0.335	1.73	0.421	1.54	0.500	1.41	0.452	1.49	0.466	1.45	0.482	1.44
2250	0.180	2.36	0.273	1.91	0.350	1.69	0.310	1.80	0.322	1.76	0.330	1.74
Initial conc. (mmols/1)	3.73		3.59		3.32		3.22		3.15		3.33	
Initial Br2 conc. (mmols/1)	3.17		3.17		3.17		3.17		3.17		3.17	
Slope* (X 10^4 Sec.)	3.90		3.00		1.55		2.45		2.10		2.05	

*From plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman Model DU

Kinetic Run #45a

Time	cis para F		cis para Cl		trans para H		cis meta Cl		cis para H		cis para CH_3O	
(seconds)	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$	A	$1/\sqrt{A}$
0	0.664	1.23	0.664	1.23	0.660	1.23	0.668	1.22	0.670	1.22	0.660	1.23
400	0.610	1.28	0.620	1.27	0.605	1.28	0.618	1.27	0.612	1.28	0.540	1.36
850	0.528	1.37	0.545	1.35	0.500	1.41	0.552	1.34	0.520	1.39	0.421	1.54
1200	0.464	1.47	0.484	1.44	0.430	1.53	0.498	1.41	0.456	1.48	0.340	1.71
1650	0.395	1.59	0.419	1.54	0.355	1.68	0.433	0.52	0.382	1.62	0.264	1.98
Initial conc. (mmols/1)	3.15		3.33		3.59		3.32		3.22		3.73	
Initial Br2 conc. (mmols/1)	3.17		3.17		3.17		3.17		3.17		3.17	
Slope* (X 10^4 Sec.)	2.23		1.83		2.90		1.63		2.35		3.80	

*From plot of $1/\sqrt{A}$ vs. time

Absorbance measurements made on Beckman DU

Kinetic Run #46

Time	cis meta Cl		cis para H		cis para F		cis para CH_3O		cis para Cl	
(seconds)	A	$\sqrt{A}$	A	$\sqrt{A}$	A	$\sqrt{A}$	A	$\sqrt{A}$	A	$\sqrt{A}$
0	0.593	0.770	0.600	0.775	0.595	0.771	0.633	0.790	0.601	0.776
100	0.575	0.759	0.580	0.762	0.568	0.754	0.580	0.762	0.586	0.765
500	0.515	0.719	0.510	0.715	0.500	0.707	0.476	0.690	0.523	0.725
850	0.470	0.685	0.454	0.674	0.454	0.654	0.390	0.625	0.477	0.690
1300	0.420	0.648	0.394	0.630	0.401	0.633	0.312	0.559	0.424	0.651
Initial conc. (mmols/l)	48.8		46.4		46.7		41.5		56.2	
Initial Br2 conc. (mmols/l)	2.89		2.89		2.89		2.89		2.89	
Slope* (X 10^4 Sec.)	0.104		0.121		0.112		0.182		0.100	
Slope/conc.	0.213		0.260		0.239		0.438		0.177	

*From plot of $\sqrt{A}$ vs. time

Absorbances measured on Beckman Model DU

Kinetic Run #47a

cis-and *trans*-1, 2-diphenylcyclopropane

Time (seconds)	1* *cis*	2 *trans*	3 *cis*	4 *trans*	5 *cis*	6 *trans*
0	0.530	0.533	0.532	0.530	0.531	0.530
616	0.364	0.341	0.363	0.335	0.365	0.339
Difference**	0.166	0.192	0.169	0.195	0.166	0.191
Initial conc. (mmols/1)	3.22	3.24	3.22	3.24	3.22	3.25

cis average = 0.167

trans average = 0.193

ratio *trans*:*cis* = 1.14:1

*Numbers refer to photolysis position

**Directly proportional to concentration

Kinetic Run #47b

Time	cis-and trans-1-(m-chlorophenyl)-2-phenylcyclopropane					
	1*	2	3	4	5	6
(seconds)	cis	trans	cis	trans	cis	trans
0	0.528	0.525	0.528	0.526	0.528	0.526
1015	0.330	0.327	0.330	0.322	0.330	0.325
Difference**	0.198	0.198	0.198	0.204	0.198	0.201
Initial conc. (mmols/1)	2.60	2.60	2.60	2.60	2.60	2.60

cis average = 0.198

trans average = 0.202

ratio trans:cis = 1.02:1

*Numbers refer to photolysis position

**Directly proportional to concentration

Kinetic Run #47c

cis-and *trans*-1-(p-methoxyphenyl)-2-phenylcyclopropane

Time (seconds)	1* *cis*	2 *trans*	3 *cis*	4 *trans*	5 *cis*	6 *trans*
0	0.527	0.550	0.535	0.550	0.527	0.550
560	0.331	0.343	0.335	0.350	0.332	0.342
Difference**	0.196	0.207	0.190	0.200	0.195	0.208
Initial conc. (mmls/1)	2.53	2.52	2.53	2.52	2.53	2.52

cis average = 0.194

trans average = 0.205

ratio *trans*:*cis* = 1.07:1

*Numbers refer to photolysis position

**Directly proportional to concentration

Appendix IV

APPENDIX IV

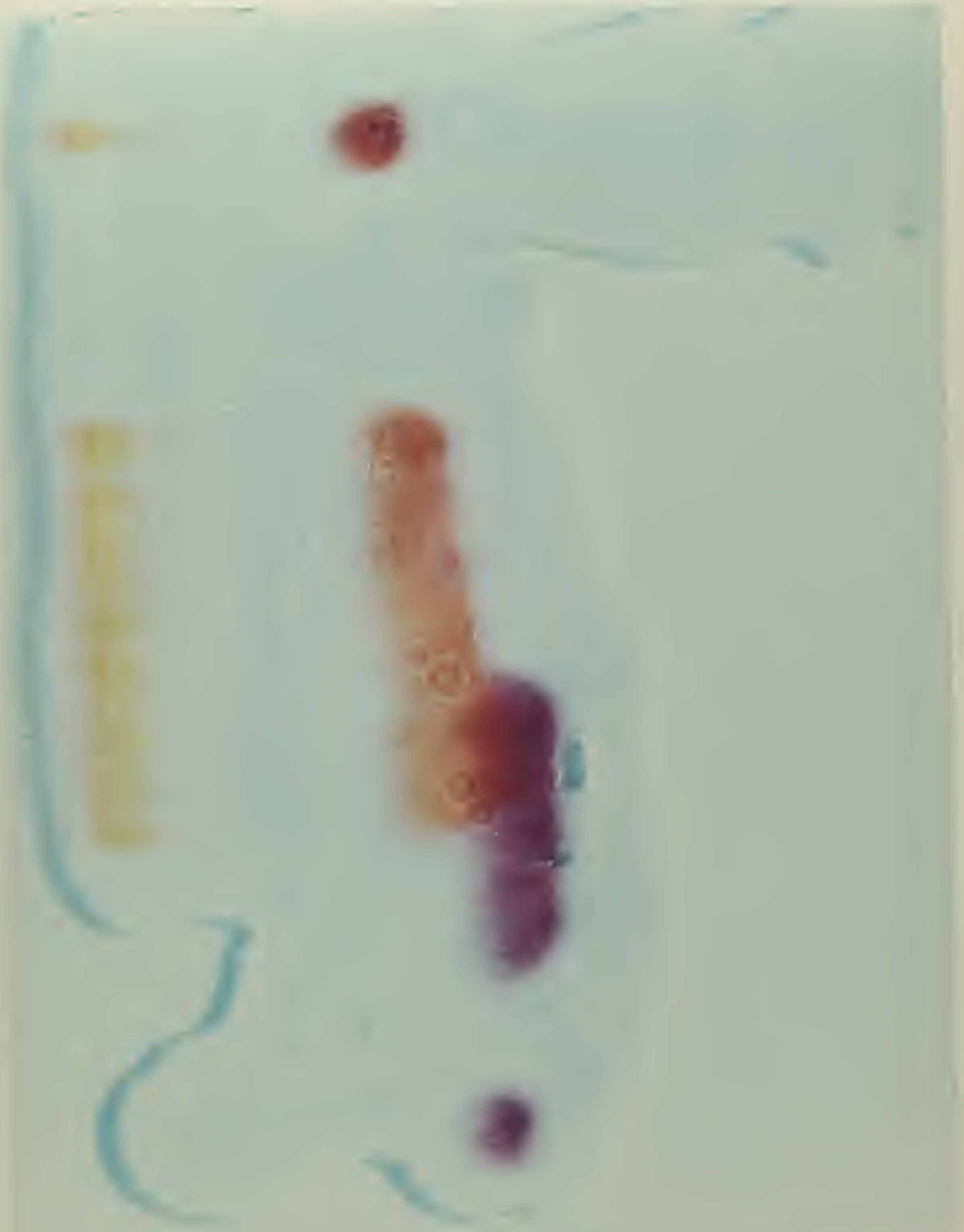
The photographs in this Appendix are reproductions of the original color negatives of two thin layer chromatograms. Each t.l.c. was prepared on 0.25 mm silica gel H plates activated at 110°C for thirty minutes. All plates were covered with a 2% formaldehyde in concentrated sulfuric acid solution after the solvent used for development was completely evaporated.

Photograph #1

The plate was streaked in three bands along the right edge of the photograph. From top to bottom these are: (1) Reaction mixture of 1, 2-diphenylcyclopropane and bromine in carbon tetrachloride; (2) pure 1, 2-diphenylcyclopropane; (3) same as 1. The plate was developed with benzene/chloroform (1/1). Both edges (top and bottom) demonstrate the presence of five minor reaction products in addition to the major reaction product. Solvent movement is from right to left.

Photograph #2

This plate was spotted on the upper right edge with the same reaction mixture as used for photograph #1 and on the lower right edge with pure 1, 2-diphenylcyclopropane. The bands were overlapped in the middle to demonstrate the separation of starting material from reaction products. A 3:1 mixture of heptane:benzene was the eluting solvent. Solvent movement is from right to left.



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1. ORIGINATING ACTIVITY *(Corporate author)*
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2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
PHOTOLYTIC RING CLEAVAGE OF 1,2-DIARYLCYCLOPROPANES WITH BROMINE IN A NON-POLAR SOLVENT

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Thesis, Ph.D., August 1966

5. AUTHOR(S) *(Last name, first name, initial)*
HOFFMANN, John Melville, Lieutenant, U.S. Navy

6. REPORT DATE
August 1966

7a. TOTAL NO. OF PAGES
193

7b. NO. OF REFS
118

8a. CONTRACT OR GRANT NO.

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. AVAILABILITY/LIMITATION NOTICES
11/6/69
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11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Bureau of Naval Personnel
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13. ABSTRACT

This work studied further the well established analogy between cyclopropanes and olefins. A series of 1,2-diarylcyclopropanes were prepared and were characterized by their ultraviolet, infrared and NMR spectra. Some of these compounds have not previously been reported.

Reactions of these compounds were studied under dark and photolytic conditions with bromine in carbon tetrachloride. No reaction was observed under dark conditions while addition of equimolar amounts of bromine took place under photochemical conditions. The addition product in all cases was the 1,3-dibromo-1,3-diarylpropane.

The kinetics of this reaction were studied at low concentrations (0.003 molar) and the influence of the para-substituent on the rates of reaction determined. The reaction rates plotted against Hammett sigma values were linear and gave a rho of -0.49 for the cis isomers and a rho of -0.44 for the trans isomers. The rate equation under these conditions was found to be

$$\text{rate} = k(\text{cyclopropane})(\text{Br}_2)^{\frac{1}{2}}.$$

A mechanism is proposed for the reaction under these conditions.

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	ROLE	WT	ROLE	WT	ROLE	WT
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